SURFACE-ALTERED HYDROPHOBIC ZEOLITES AS SORBENTS FOR HAZARDOUS ORGANIC COMPOUNDS

by

Roger E. Huddleston

Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Science in Hydrology

New Mexico Institute of Mining and Technology
Socorro, New Mexico

November, 1990

Abstract

Surface-altered zeolites were investigated regarding their ability to remove organic chemicals from aqueous and non-aqueous solutions. A natural zeolite was treated with the large organic cations hexadecyltrimethylammonium (HDTMA), and methyl-4-phenylpyridinium (MPP), to create hydrophobic surfaces. The modified zeolite surfaces remained stable in inorganic salt solutions ranging from 0.01 M to 1.0 M, pH buffers ranging from pH 3 to 10, methanol, benzene, and soltrol (a mixture of C_8 to C_{13} hydrocarbons). Solutions containing other large organic cations were effective in displacing up to 30% of the bound quaternary ammonium cations.

Batch sorption studies of phenol, ethylbenzene, 1,1,1-trichloroethane (TCA), and tetrachloroethylene (PCE), to the modified zeolites were conducted. Methanol, benzene, and 0.005 M $CaCl_2$ aqueous solutions were evaluated as solvents. In almost all cases, essentially no sorption from the organic solvents was observed. Phenol, however, was removed from benzene by both HDTMA- and MPP-zeolite. In benzene and aqueous solutions, phenol sorption isotherms fit Freundlich-type sorption models, while all other sorption isotherms were highly linear. Ethylbenzene, TCA, and PCE sorption was consistent with the octanol-water partition coefficients for these compounds, and was consistent with a partitioning mechanism into surface organic carbon. The dominant role of organic carbon in influencing sorption suggests that neither the surface-altering agent functional groups nor the zeolite molecular selectivity played a significant role in influencing sorption. Organically-modified minerals such as zeolites may be useful as clay liner and slurry wall amendments to immobilize organic contaminant releases.

Table of Contents

List of Figures

List of Tables

Acknowledgements

Funding for this project was provided by the USGS and the New Mexico Water Resources Institute under USGS grant number 14-08-0001-G1657. Without this funding I could not have been a part of this project.

Thanks to my advisor, Rob Bowman, for useful comments, criticisms, and discussions on all aspects of the research throughout the project duration. Doug Ming's expertise on zeolites was invaluable, as was Jake Turin's expertise on gas chromatography and other laboratory techniques. Thanks to Don Brandvold in the Chemistry Department and Lynn Brandvold in the Bureau of Mines for suggestions about analytical methods and use of their facilities.

Finally, a thanks to all the hydrology graduate students who have helped to make this situation bearable, and even fun at times. Special thanks go to Mike Wei, for general discussions on anything from research to hockey; Jake Turin (again) for maintaining my sanity by the use of insane puzzles; and Rolf Schmidt-Petersen, for being a terrific roommate and officemate. Last but certainly not least, thanks to Donna Twickler for her love, patience, and understanding.

I.

INTRODUCTION

In recent years, increasing attention has been focused on the nature of hydrophobically altered clays and their applications. Although such materials are known to have been in existance for many years, recent nationwide concern about hazardous waste disposal practices and releases has stimulated increased research in this area. While the existance of naturally-occurring hydrophobic soils is well documented, (DeBano and Letey, 1969; DeBano, 1981; Hendrickx et al., 1988; van Dam et al., 1990), most recent research has focused on characterization of laboratory-modified clay minerals (Bouchard et al., 1988; Boyd et al., 1988a, 1988b, 1988c; Cadena, 1988, 1989; Cadena and Jeffers, 1987; Jaynes and Boyd, 1990; Jaynes et al., 1989; Mortland et al., 1986; Smith et al., 1990; Wolfe et al., 1985, 1986). This research project is an effort to expand on the recent body of literature regarding the characterization of surface-modified minerals.

The need for research in this area was summarized nicely by Wilson (1988). As Wilson discusses, potential environmental problems associated with hydrophobic soils include golf course management, agricultural management, flooding and erosion control over burned chaparral lands, petroleum recovery, and hazardous waste recovery following uncontrolled releases at disposal sites. In addition to increasing our understanding of properties of hydrophobic soils, such materials can have potential engineering applications. These applications, discussed in detail by Alther et al. (1990), include uses of hydrophobic clay materials for waste stabilization, water treatment, spill control, tank liners, and landfill liners.

The primary goal of this project was to determine the sorptive properties of a hydrophobically altered zeolite with regard to different organic solutes. This goal is most directly related to applications in hazardous waste remediation. When the hydrophobic nature of soil and aquifer materials is altered, via either natural or anthropogenic mechanisms, the sorptive properties for organic contaminants can be significantly altered. Therefore, it is necessary to evaluate the effect of different hydrophobic mineral treatments, in an attempt to determine the factors influencing these changes in sorptive properties. To meet this goal, a variety of surface-modifying agents were evaluated to determine their effect on altering surface sorptive properties.

In addition, many hazardous waste releases involve large volumes of organic liquids. These organic solvents may impact the extent of dissolved organic solute sorption. To evaluate this effect, sorption studies were conducted not only from aqueous solutions, but also from a polar and a nonpolar organic liquid. The sorption of a variety of organic solutes was evaluted, primarily to evaluate the effect of different functional groups on the extent of sorption.

In summary, this research project was developed based on the hypothesis that organic solute sorption to mineral surfaces behaves differently depending upon several different factors. These factors are: the degree and stability of mineral surface hydrophobicity; the nature of the chemical causing mineral surface hydrophobicity (degree of carbon loading on the mineral surface, alkyl vs. phenyl functional groups); solute polarity/functional nature (alkyl vs. phenyl groups); and solvent composition and polarity.

Several study objectives were defined to test this hypothesis. These were:

1. To create a variety of hydrophobic mineral surfaces and quantify the degree of hydrophobicity.
2. To determine the surface stability of this modified mineral.
3. To quantify organic solute sorption to the hydrophobic surfaces from aqueous and nonaqueous solvents.

While most previous studies on surface modification have employed clay minerals, a natural zeolite was chosen as the mineral sorbent for this project. A zeolite mineral was chosen because the natural high cation exchange capacity (CEC) of zeolites makes them amenable to surface modification using organic cations. This type of mineral can exist naturally with a relatively large particle size, which facilitates column leaching studies. Pure clay minerals are often so fine textured that column experiments are not practical. The material used for this study provided an easily characterizable analogue for natural clay-containing, ion-exchanging soil. Although column studies were ultimately not conducted as part of this project, these results and this zeolite can be used as a foundation for future work, including column experiments.

The specific materials and methods used to meet these objectives are defined in a later section of this report. However, to put the scope and background of this project in perspective, it is appropriate to develop an understanding and appreciation of general sorptive properties of both natural soil materials and laboratory-altered hydrophobic materials. In addition, zeolite structure and chemistry are quite different from other silicate minerals, so a review of these unique properties is also appropriate. Therefore, before proceeding with the details of this particular project, detailed background discussions on these subjects directly follow.

II.

PREVIOUS WORK

GENERAL TREATMENT OF SORPTION DATA TO NATURAL SOILS

Sorption of organic compounds to natural, organic matter-containing soils has been thoroughly documented (Chiou et al., 1983; Greenland, 1965; Hamaker and Thompson, 1972; Karickhoff et al., 1979; Mortland, 1970; Schellenberg et al., 1984; Theng, 1974; Wu and Gschwend, 1986). Because the emphasis of this project was on organic compound sorption to treated materials rather than natural soils, details of these studies will not be presented. Rather, generalities of organic compound sorption that apply to both treated and untreated soils will be discussed.

The most common method of analyzing sorption data is via the sorption isotherm. Data for sorption isotherms must be collected at equilibrium, and at constant temperature and pressure. It may be necessary to correct for secondary reactions such as precipitation, or other interferences, especially when the sorption of ionic compounds is evaluated. Although many isotherm shapes have been observed, the most commonly evaluated shapes for aqueous solution sorption are the linear, Langmuir, and Freundlich types (Bohn, et al., 1985).

The linear isotherm is often seen with sorption of low-solubility organic compounds to soils. This isotherm is described by the equation:

$$S = K_d C \qquad [2\text{-}1]$$

where:

S = Mass of solute sorbed to substrate, [mg/kg]

K_d = Distribution coefficient, [L/kg]

C = Equilibrium solution concentration, [mg/L]

A plot of S vs. C will yield a straight line of slope K_d if sorption can be described by the linear isotherm. The linear form of the isotherm implies the sorbent has infinite capacity to retain dissolved species. This is in fact rarely the case, and this linear form is usually valid only at low solute concentrations.

The Langmuir isotherm can be described by an equation of the form:

$$S = \frac{K_L C m}{1 + K_L C} \qquad [2\text{-}2]$$

where, in addition to variables already defined:

K_L = Langmuir constant, [L/kg]

m = Maximum amount of solute that can be sorbed in a complete monolayer [mg/kg]

This equation was derived assuming energy of sorption is constant and independant of surface coverage, solute molecules do not interact, adsorption is on specific sites, and maximum sorption is reached when a complete monolayer is filled on the adsorbent. Note that when concentrations are low, especially relative to the maximum number of surface sorption sites, $K_LC \ll 1$, and the equation reduces to a linear form. This is most probably the case for most low-solubility organic compounds; the number of organic molecules in solution is so low that the number of available sorption sites is effectively infinite, resulting in linear isotherms.

The Langmuir isotherm is often linearized in the form:

$$\frac{C}{S} = \frac{1}{K_L m} + \frac{C}{m} \qquad [2\text{-}3]$$

such that a plot of C/S vs. C will result in a straight line with slope 1/m and intercept $1/mK_L$.

The Freundlich isotherm is described by the equation:

$$S = K_F C^N \qquad [2\text{-}4]$$

or, in the linearized form:

$$\log S = N \log C + \log K_F \qquad [2\text{-}5]$$

where, in addition to previously defined variables,

N = Empirical constant, [-]

K_F = Freundlich constant, [L/kg]

The Freundlich equation is used primarily as an empirical equation, but with the proper set of assumptions, it can be theoretically derived. In contrast to the Langmuir equation, the Freundlich equation implies that an infinite number of sorption sites are available, and that energy of sorption decreases logarithmically as surface coverage increases. Care must be used when comparing Freundlich constant and N values from different studies, because the values of these constants are highly dependant upon the system of units used. Note that when the value of the constant N = 1, the equation is reduced to a linear form.

It has been well documented that the amount of organic matter in a soil often controls the extent of nonionic nonpolar organic compound sorption (Chiou et al., 1979). As a result, the linear partition coefficient is often normalized by the amount of organic matter in the soils, giving an organic matter partition coefficient, K_{om}:

$$K_{om} = \frac{K_d}{f_{om}} \qquad [2\text{-}6]$$

where f_{om} is the fraction of organic matter in the soil. If the fraction of organic carbon is used, the corresponding coefficient is designated K_{oc}. While K_d values can vary over several orders of magnitude for different soils, the normalized K_{om} or K_{oc} values often vary within only a factor of 2 for any given compound (Gschwend and Wu, 1985).

This dominant role of organic carbon in controlling the extent of nonionic, nonpolar organic compound sorption has been cited as evidence supporting a partitioning type of sorption mechanism of the organic compound into soil organic matter (Chiou et al., 1979). Other data cited by Chiou et al. in support of a partitioning mechanism include: linear isotherms even at concentrations approaching the aqueous solubility of many compounds, a linear relationship between K_{oc} and aqueous solubility, and a strong correlation between the octanol-water partition coefficient (K_{ow}) and K_{oc}.

Despite the dominant role of organic carbon in influencing sorption of organic compounds, natural materials containing very little or no organic carbon have an almost negligible capacity for nonionic organic compound sorption. Low molecular weight nonionic organic compounds ($<$150 amu) are usually not sorbed at all to natural materials, because of the limited potential of the molecule for Van der Waals, ion-dipole, or other interactions with the mineral surface (Greenland, 1965). Mortland (1986) reported that aromatics, and particularly halogenated aromatics, were sorbed only slightly, if at all, to pure clay minerals from aqueous solutions. Sorption of many other small organic compounds to pure clays saturated with inorganic cations has been found to be zero or negligible (Boyd et al., 1988b; Smith et al., 1990). However, exchanging organic cations onto the mineral surface to expand clay layers and create a hydrophobic medium has increased sorption of nonionic organic compounds by as much as 2 orders of magnitude over identical untreated materials (Bouchard et al., 1988).

SUMMARY OF RESEARCH ON LABORATORY-ALTERED HYDROPHOBIC SOILS

Because of this large increase in sorption capacity of modified soils over untreated soils, many investigators have recently turned to evaluating hydrophobic laboratory-altered clays as sorbents for organic compounds. The first hydrophobically altered clay was reportedly created by Smith (1934) (cited in Weiss, 1963). Since that time, researchers have investigated the properties of clays and soils altered with a variety of organic cations, amines, chlorosilanes, polymers, and other classes of organic structures. Such altered clays are often referred to as organo-clays. Clays and soils treated in such a manner have been investigated with regard to their engineering properties (Brandt, 1969), swelling properties (Jordan, 1949), sorptive properties, infiltration and hydraulic properties (Letey et al., 1975), even for their use in the cosmetics industry (Jordan, 1963), as well as for numerous other applications. Because this project focused on the sorptive properties of hydrophobically altered minerals, this section will concentrate on studies of organo-clays designed to investigate these sorptive properties.

Much of the early work on organo-clays was conducted by Barrer and others in the late 1950's and early 1960's. Barrer and his colleagues created a large number of hydrophobic clays by treating montmorillonites with amines, ranging from primary amines to quaternary amines, and including diamines. Many of these studies concerned the modified clay swelling and layer spacing in a variety of organic liquids (Barrer and Brummer, 1963; Barrer and Millington, 1967). Concurrent studies were conducted by Weiss, who, over the course of 5 years, studied over 8000 derivatives of layer silicates to evaluate the basal spacing and swelling properties of these minerals (Weiss, 1969). A general conclusion reached in all these papers was that while natural expandable clays will swell in aqueous solutions as water solvates inorganic cations, organo-clays will not. Rather, while some interlamellar clay expansion is caused by the exchange of the large organic cation itself, considerable further swelling occurs in organic solvents but not in water. These studies showed that the exchange of organic cations onto clay surfaces effectively imparts an organophillic coating to the surface.

Much of Barrer's work also included sorption studies of organic compounds to these organo-clays (Barrer and Brummer, 1963; Barrer and Hampton, 1957; Barrer and MacLeod, 1955; Barrer and Millington, 1967; Barrer and Perry, 1961a, b; Barrer and Reay, 1957). This work, which focused on organic compound sorption from the vapor phase, included the generation of sorption and desorption isotherms (Barrer and Brummer, 1963; Barrer and MacLeod, 1955), determination of organo-clay selectivity for 11 different compounds (Barrer and Hampton, 1957), and evaluation of competitive sorption from binary vapor mixtures (Barrer and Hampton, 1957; Barrer and Perry, 1961a, b). A significant conclusion from all of this work was that interlamellar expansion is required for alkylammonium exchange onto clay surfaces. When a clay interlamellar region expands, the entire interlamellar area will be saturated with organic cations before another interlamellar region will expand. Thus if organic cations are added at concentrations below the clay CEC, the resulting mixture will contain clay particles saturated completely with organic cations, and clay particles saturated completely with inorganic cations, but no clay particles saturated with both organic and inorganic cations (Barrer and Brummer, 1963). In addition, Barrer noted that benzene sorption was highest on clays saturated with short chain organic cations (Barrer and Millington, 1967), a conclusion tested and later confirmed by McBride et al. (1977), Cadena (1988), and Jaynes and Boyd (1990), for benzene sorption from aqueous solutions. Finally, Barrer found that desorption of essentially all organic vapors was hysteretic.

It has only been within the past 10 to 15 years that researchers have begun looking at the sorption of organic contaminants to these modified clays from aqueous and other solutions. With increased attention being focused on pollutant transport and retardation in the late 1970's and 1980's, people have begun to evaluate the use of organo-clays as possible sorbents for organic chemicals released to the environment in groundwater aquifers. Because these environments are aqueous, the majority of this recent research has focused on organic compound sorption from aqueous solutions. Very little work has been done on investigating the desorption of sorbed organic cations, or on evaluating organic solute sorption from non-aqueous solvents.

Organo-Clay Complex Synthesis

The modified clay surface is typically synthesized by mixing a solution containing an appropriate amount of organic cation with a specific mass of clay saturated with inorganic cations, often sodium. Most researchers have found that there is a quantitative exchange of the large organic cation up to the clay CEC (Bouchard et al., 1988; Boyd et al., 1988a, 1988c; Cowan, 1963). However, sorption of some large organic cations can occur above the CEC (Wolfe et al., 1985). As a result, the organic cation is usually added in an amount equal to the clay CEC. Cadena (1988) found that adding tetramethylammonium (TMA) in excess of the CEC actually caused a decrease in benzene sorption from solution. The decreased sorption was thought to be due to a combination of two factors: excess TMA took up sorption sites on the modified clay, thus reducing the number of sites available for benzene sorption; and excess TMA ions in solution solvated the benzene molecules, thus reducing the propensity for benzene to be removed from solution.

Organo-Clay Complex Stability

Thermodynamic Principles

Once the modified surface is created, most researchers have stated that sorption is apparently irreversible, or that it is very difficult to displace the sorbed organic cation, without presenting supporting experimental data (Boyd et al., 1988a; Cadena, 1988; McBride et al., 1977). Thermodynamic principles and some thermodynamic data, however, can be used to explain why the sorption of these large organic cations is essentially permanent. Hayes et al. (1978) measured the sorption enthalpy of 13 different large pyridinium compounds to sodium montmorillonite. They found exothermic sorption in all cases, with sorption enthalpies ranging from -10 kJ/mole to -48 kJ/mole. Typical sorption enthalpies of inorganic cations are less than -8 kJ/mole, but may be as high as -42 kJ/mole (Helfferich, 1962). Therefore, while sorption of large organic cations is generally thermodynamically favored over the sorption of inorganic cations, desorption of these organic cations would not be thermodynamically favored unless the heat generated by the replacing cations was enough to compensate for the endothermic desorption of the large organic cations.

It is probably reasonable to assume that the sorption of other large organic cations is thermodynamically similar to the sorption of these large pyridinium cations. Once sorbed, the organic cations may be held to the surface by not only charge, but by other forces such as hydrogen bonding, Van der Waals forces, ion-dipole, and other physical forces, depending on the molecular weight, functional groups, and configuration of the molecules (Boyd et al., 1988a; McBride et al., 1977).

Not only sorption enthalpy, but solution entropy also contributes to the essentially irreversible nature of large organic cation sorption. Sorption of one large molecule results in the displacement of several water molecules from a mineral surface, thus increasing the overall system entropy (Greenland, 1965; Mortland, 1970; Theng, 1979). Additionally, water free of hydrophobic compounds generally exists in a loosely structured form, dominated by hydrogen bonding and loose solvation shells around inorganic ions. When a hydrophobic molecule is introduced to the solution, water forms a rigid, ice-like cage structure around the molecule, reducing the bulk solution entropy (Hamaker and Thompson, 1972). When hydrophobic molecules are sorbed to mineral surfaces, interactions with the mineral surface and with adjacent hydrophobic groups results in a partial break-down of the rigid water structure, thus resulting in a favorable change in solution entropy.

Experimental Data

Although these thermodynamically based arguments are strong support for irreversible organic cation sorption to clays, very little experimental data have been presented to validate this theory. Jordan (1963) examined the desorption of dioctadecyldimethylammonium ions (DODDMA) sorbed to montmorillonite up to the clay CEC in n-hexane and isopropanol. He found that n-hexane caused desorption of about 4.4% of the originally sorbed DODDMA, and isopropanol could remove an additional 11-13% of the originally sorbed DODDMA. In a similar study, Slabaugh and Hanson (1969) reported that a 48 hour Soxhlet extraction of DODDMA-hectorite in isopropanol resulted in about a 10% decrease in organic carbon content of the modified clay. Jordan (1963) theorized that one of two processes may have been responsible for the observed organic cation removal: i) the amount removed represented cations not actually exchanged on the surface, but those sterically hindered from sorbing to exchange sites that were therefore only weakly hydrophobically bonded to surface-bound chains, or ii) that "reaction energies diminish as the negative charges of the clay lattice become progressively neutralized, and that a minor proportion of organic cations will be removable with low energy solvents" (p. 304). In other words, as the surface charge is satisfied, the cations become more weakly bound, and can be removed. While theory i is certainly possible, theory ii seems unlikely, since the organic cations are not neutralizing a surface charge imbalance, they are replacing other inorganic cations sorbed to the surface (so the surface charge imbalance is already neutralized). Unless there were some other cationic species dissolved in the organic solvent, (which in itself is unlikely), to replace the desorbing organic cation, it seems the condition of surface electrical neutrality would not be met and the organic cation would not desorb.

Other studies have evaluated the desorption of organic cations by replacement with other cations. Mortland (1970) reported that amino acids in the cationic state were sorbed to clays and were not removed with water or solvent washes, but could be removed with concentrated salt solutions. Theng (1974), however, has reported that the sorption of amino acids is extremely pH dependant, and as such they are not strongly sorbed except at very low pHs; so it is not surprising that high cation concentrations were effective in removing the amino acids in approximately neutral solutions. The specific amino acids evaluated, rinsing solution pH's, and extent of desorption were not reported in Mortland's review. In a series of studies, McAtee (1962, 1963), and McAtee and Hackman (1964), evaluated the replacement of dimethylbenzyllaurelammonium ions (DMBL) added to clay up to the CEC, with a series of primary to quaternary amines ranging from C_2 to C_{18}, in an organic solvent (80% iso-octane and 20% isopropanol). The maximum DMBL desorption occurred with diethylammonium added at 3x the clay CEC, where 82% of the originally sorbed DMBL was removed. In general, the more basic amines were more effective at replacing DMBL, and larger ions were less effective than smaller ions. This was thought to be because the larger ions were sterically hindered from fully exchanging with the sorbed species. In essentially all cases, however, a large excess above the clay CEC was required to cause appreciable desorption of the

DMBL. Although these few experiments are in agreement with theoretical principles, a larger database is lacking. Therefore, one goal of this project was to gather experimental data to evaluate the thermodynamic argument that large cations, once sorbed, are essentially permanently bound.

Organic Solute Sorption to Organo-Clays from Aqueous Solutions

At least 28 different organic cations have been evaluated as surface-altering agents for sorption studies of organic chemicals from aqueous solutions alone. Many other organic cations have been exchanged on clays for swelling and other studies. For these sorption studies, at least 32 different nonionic organic compounds have been studied for sorption properties to different organo-clays. Most studies have been conducted using smectite clays as the mineral sorbent. However, many studies have used other clay minerals and natural soils for surface-altering treatments. The following discussion details the major conclusions of these studies.

As discussed previously, the exchange of organic cations to smectite surface usually results in a corresponding expansion of the clay lamellae. Cowan and White (1962) showed that as the chain length of exchanged primary ammonium cations increased from 2 to 18 carbons, the clay layer spacing increased. In contrast, McBride et al. (1977) found that TMA ions more effectively separated clay layers than tetraethyl- (TEA) or tetrapropylammonium (TPA) ions. They theorized that the TMA tetrahedron is rigid and holds layers apart, while TEA and TPA ions are flexible and tend to lie parallel to clay layers, thus effecting no appreciable layer separation.

This change in layer spacing as a function of the surface-altering agent structure has been found to create a selective surface that sorbs some molecules but not others (Cadena and Jeffers, 1987; McBride et al., 1977). In particular, TMA-clays have been found to show a pronounced selectivity for benzene and phenol, but will not sorb toluene, xylene, or chlorobenzenes (Cadena and Jeffers, 1987; McBride et al., 1977). In this case, the clay layers are not separated far enough to allow the intercalation of molecules larger than benzene or phenol. In many cases, however, intercalation of organic solutes results in additional layer expansion (Cowan and White, 1962; Mortland et al., 1986; Stuhl et al., 1979; Wolfe et al., 1985, 1986). However, because hydrophobic organic solute sorption may not necessarily be exothermic, if additional layer expansion is necessary for solute sorption, the energy required for layer expansion may be more than that provided by sorption, and the species will not sorb (Cowan, 1963). Thus different clay treatments are often effective at sorbing specific species.

Short-chain surface-altering organic cations may not completely cover the mineral surface, thus leaving part of the mineral surface exposed (Cowan and White, 1962; Boyd et al., 1988c; Mortland et al., 1986). When the organic sorbates are polar, usually alcohols or amines, both the mineral surface and the surface-altering agent organic chain may contribute to sorption (Cowan and White, 1962; Mortland et al., 1986; Slabaugh and Hanson, 1969; Stuhl et al., 1979; Wolfe et al., 1985). Because water molecules strongly solvate the mineral surface, small polar molecules cannot effectively compete for mineral sites and are often not sorbed from aqueous solutions when the surface-altering agents are small (Boyd et al., 1988a, 1988b, 1988c; Cadena and Jeffers, 1987; McBride et al., 1977). Some polar organics, such as hexanol, octanol, phenol, and chlorophenols, can compete with water for mineral sites, and often are weakly sorbed initially, followed by increased sorption when the sorbed hydrophobic molecules interact with dissolved sorbate molecules. This phenomenon has been observed and is characterized by S-shaped sorption isotherms (Boyd et al., 1988c; McBride et al., 1977; Mortland et al., 1986; Stuhl et al., 1979).

Generally, larger, more hydrophobic molecules are more strongly sorbed to clays treated with larger organic cations that fully cover the mineral surface. While chain lengths longer than three carbons may often increase layer spacing, a simple increase in organic cation chain length may not always result in increased sorption. The long organic tails may sterically hinder sorbate access to interlamellar sorbent sites, or in the case of polar molecules, may cover additional mineral surface sorption sites (Boyd et al., 1988b; Cadena 1989; Cowan and White, 1962; Jaynes and Boyd, 1990; McBride et al., 1977). Alternately, long diprotonated ions, such as diamines, may tie clay layers together and prevent further layer expansion that could allow solute sorption (Wolfe et al., 1985).

In general, however, these larger, more hydrophobic cations increase the sorption capacity for most compounds. A partitioning type of mechanism into the hydrophobic medium created by large surface-altering agents often describes sorption of organic compounds to organo-clays. When organic sorption to the organo-clay is normalized by the organic matter content as a K_{om}, (Eq. [2-6]), the resulting K_{om} values are often very similar to the K_{ow}'s for the compounds. This is often cited as evidence supporting a partition-type mechanism of sorption (Boyd et al., 1988a, 1988b, 1988c; Jaynes et al., 1989; Toro-Suarez et al., 1990).

When sorption to natural soils is normalized by a K_{om} and compared to the K_{om} for the same compound sorbed to an organo-clay, the K_{om} values for the organo-clay complexes are often ten to thirty times higher (Boyd et al., 1988a, 1988b, 1988c; Toro-Suarez et al., 1990). Typically, K_{om} values for a given compound vary between different soils by much less than a factor of ten (Gschwend and Wu, 1985). The higher K_{om} values of organo-clays are attributed to the fact that natural soil organic matter contains many polar alcohol, ketone, amine, and other functional groups, while the surface-altering agent functional groups are usually straight chain hydrocarbons without polar functional groups, and thus the latter act as a much more effective partitioning medium for nonpolar organic compounds. Whether the functional groups on the surface-altering agents are primarily alkyl or aromatic in nature appears to be less important than the total amount of organic carbon and chain length of the molecule in affecting sorption of hydrophobic organic solutes (Smith et al., 1990).

Organic Solute Sorption to Organo-Clays from Organic Solvents

Only two studies were identified that evaluated organic chemical sorption to organo-clays from nonaqueous solvents. Slabaugh and Hanson (1969) studied the sorption of polar organic compounds from toluene, primarily to evaluate the formation of clay-organic gels. As such, the parameters they determined are not directly applicable to evaluating the transport of organic compounds dissolved in organic solvents. Mortland et al. (1986) evaluated the sorption of phenol and several chlorinated phenols to a variety of surface-altered smectites from hexane and water. In general, they found higher phenol species sorption from hexane than from water. This was attributed to a difference in solvent-solute interactions. In water, phenolic compounds have a strong interaction with the solvent via hydrogen bonding, and are not as strongly removed from solution. In hexane, these compounds have relatively little interaction with the solvent and are sorbed.

Although these studies provide some information on the behavior of organic species dissolved in organic solvents, much data are lacking, especially data on the sorption of nonpolar organic compounds to modified mineral surfaces from organic solvents. Many organic compound releases involve both aqueous and organic phases, and solutes may travel for large distances in an organic phase before entering the aqueous phase (Wilson et al., 1990). The solutes of interest will sorb much differently when dissolved in an organic phase rather than the aqueous phase. For this reason, it is desirable to know the sorption characteristics of organic chemicals when in an organic phase. Because there is a notable lack of data in this area, one objective of this project was to collect data on this subject.

Table 2-1 details the specific surface-altering agents and organic solutes used by each of the authors cited above.

Table 2-1. Summary of Sorption Research on Organo-clays. Abbreviations are identified in Appendix A. All experiments were conducted in aqueous solutions unless otherwise noted.

Reference	Sorbent	Solute	Comments
Bouchard et al., 1988	EHDDMA-soil	toluene naphthalene diuron	Sorption to treated soils as much as 100x higher than to untreated soils.
Boyd et al., 1988a	HDTMA-soils	Benzene DCB PCE	Linear sorption, HDTMA 10-30x more effective than natural OM at removing organics.
Boyd et al., 1988b	HDTMA-smectite	Benzene TCE	Linear sorption, included partially saturated HDTMA-clays.
Boyd et al., 1988c	smectites with: DODDMA HDTMA HDP PTMA TMA 4-MP	PCP	Higher sorption to clays having more hydrophobic altering agents.

Table 2-1. Summary of Sorption Research on Organo-clays. Abbreviations are identified in Appendix A. All experiments were conducted in aqueous solutions unless otherwise noted.

Reference	Sorbent	Solute	Comments
Cadena and Jeffers, 1987	TMA-bentonite	benzene toluene o-xylene chloroform	Determined clay selectivity, benzene most preferred.
Cadena, 1988	AC, and TMA-bentonite TMA-soils	benzene toluene o-xylene chloroform	Linear and Freundlich isotherms best fit data. K_d on clay was 100x higher than soils for benzene. AC most effective, but not selective.
Cadena, 1989	TMA-bentonite	benzene toluene o-xylene	Same as Cadena and Jeffers, 1987.
Cowan and White, 1962	Montmorillonite with: C_n primary amines $n = 2, 4, 6, 8,$ $10, 12, 14, 16, 18$	Phenol o, m, p-cresol catechol resorcinol hydroquinone	DDA most effective, giving the best layer separation with least steric hinderence.
Cowan, 1963	DDA-bentonite TDA-bentonite	phenol m-cresol	Exothermic solute sorption, Freundlich isotherms best fit.
Jaynes et al., 1989	HDTMA on: vermiculite smectite illite kaolinite	benzene toluene ethylbenzene	High-charge clays more effective than low-charge clays at retaining BTE. K_{om} and K_{ow} values were very similar.
Jaynes and Boyd, 1990	Clays with: TMA PTMA HDTMA	benzene toluene ethylbenzene p-xylene butylbenzene naphthalene	TMA most effective benzene sorbent, but less effective at sorbing larger compounds.
McBride et al., 1977	smectite with: TMA TEA TPA HA HDTMA-hectorite	benzene phenol o-DCB 1,2,4-TCB	Higher benzene than phenol sorption, due to H-bonding. All sorbents less effective than AC. HDTMA effective at removing chlorobenzenes, TMA is not.

Table 2-1. Summary of Sorption Research on Organo-clays. Abbreviations are identified in Appendix A. All experiments were conducted in aqueous solutions unless otherwise noted.

Reference	Sorbent	Solute	Comments
Mortland et al., 1986	smectite with: HDP HDTMA PTMA TMA	phenol chlorophenol dichlorophenol trichlorophenol	From water and hexane. greater sorption with more Cl. Generally higher sorption from hexane, possibly due to greater clay swelling in hexane.
Slabaugh and Hanson, 1969	DODDMA-hectorite	nitromethane acetone 2-butanone methanol ethanol n-propanol isopropanol n-butanol	From toluene only. Determined sorption selectivity in the order presented (nitromethane most preferred, butanol least preferred).
Smith et al., 1990	bentonite with: TMA TEA BTMA BTEA DDTMA TDTMA HDTMA BDMHDA	CCl_4 TCE (in competition with CCl_4 only)	Larger organic cations behave more like OM than smaller cations.
Stul et al., 1979	montmorillonite with: C_n primary amines $n = 6, 8, 10, 12, 14, 18$	butanol hexanol octanol	Weak sorption due to competition with water.
Toro-Suarez et al., 1990	HDTMA-soil	benzene toluene naphthalene	Reasonable K_{om}-K_{ow} correspondance. Treated soil 10x more effective than natural OM at removing organics.
Wolfe et al., 1985, and Wolfe et al., 1986	Bentonite with: PA DDA DDDA	butanol hexanol octanol benzene toluene nitrobenzene phenol chloroform dimethylphthalate acetaldehyde acetone	No intercalation of any organics on DDDA clay. Theorize layers are tied together and cannot expand to accept other molecules.

REVIEW OF ZEOLITE PROPERTIES

As discussed in section I, clay minerals were not evaluated as sorbents in this project. Rather the natural zeolite clinoptilolite was used. Like clays, zeolites are characterized by high surface areas and high CECs. In contrast to the commonly used smectite clays, however, zeolites are not expandable layer silicates; they are rigid, three-dimensional framework structures. This combination of rigid structure with clay-like surface area and CEC is a result of several unique zeolitic properties worthy of review.

Zeolites are tectosilicate minerals, combinations of silica and alumina tetrahedra linked together in three-dimensional networks. Because Al^{3+} is a part of the crystalline structure only as a result of isomorphous substitions for Si^{4+}, all aluminum ions are tetrahedrally coordinated. The property specific to zeolites is that the tetrahedra are bound in rings of 6, 8, 10, or 12 tetrahedra, creating open channels that penetrate into the mineral structure. The more tetrahedra forming the ring, the larger the channel openings. The channels may penetrate in 1-D, 2-D, or 3-D networks, although they are not always interconnected in three dimensions. This means that a molecule entering a 1-D channel network can move only in a line, while a molecule entering a 2-D channel network can move in a plane, and a molecule entering a 3-D network can move to any point within the channel system. However, because channels in different directions may be different sizes, a 3-D network for a small molecule may be reduced to only a 2-D or 1-D network for a larger molecule that is excluded from the smaller openings.

Because of this large network of internal channels, zeolites have an extremely large specific surface area, up to 800 m^2 per gram (Newsam, 1986). Because the surface area is large, and because Al^{3+} will substitute for Si^{4+} in the tetrahedra, a large negative charge arises on the exposed surfaces. This negative charge is counterbalanced by exchangable cations. As a result, natural zeolites have hydrophilic surfaces with an extremely high CEC, up to 300 me/100 g (Ming and Mumpton, 1989). Due to this unique channel structure, however, over 99% of the zeolite surface, and corresponding CEC, is in the interior of the mineral structure (Newsam, 1986).

In addition to the silica and alumina tetrahedra and exchangable cations, water is a part of the zeolite mineral formula. The water molecules are not part of the crystalline framework, but are loosely held in solvation shells around cations within the internal channels. Because the channels are so small, surface tension forces prevent the water from evaporating under normal ambient conditions. However, water may be driven off from the mineral when heated to temperatures near 500°C (Barrer, 1978). Thus the name zeolite, ("zein", to boil, and "lithos" stone), was derived from the odd appearance of boiling the minerals gave when heated (Ming and Dixon, 1987a).

It is this combination of channel structure, high surface area, high CEC, and removable water that makes zeolites useful for a number of unique applications. One of the more thoroughly investigated zeolite properties is their use as molecular seives. Because the zeolitic channels are only a few angstroms in diameter, some molecules will enter the channels and be retained within the zeolite structure, while larger molecules will be impeded from entry and can pass by. This phenomenon is known as molecular seiving. This molecular seiving effect is generally most efficient on dehydrated zeolites. Dehydrated zeolites have been employed in this manner to separate branched chain isomers of alkanes from straight chain isomers, and to separate different xylene isomers. Because different zeolite minerals have different channel dimensions, the proper mineral can be specifically chosen for the desired separation.

Somewhat related to molecular seiving is hydrocarbon cracking widely used in oil refining. Cracking is the process whereby heavy, long-chain hydrocarbons are filtered through zeolite packs and cracked, or broken, into the smaller hydrocarbons that eventually make up gasoline (Kerr, 1989). In contrast to clay minerals, which can also be used for cracking, the molecular seiving property of zeolites selectively allows only specific compounds to enter the channels to be subsequently catalytically cracked by the zeolite. This application has stimulated an active area of research within the petroleum industry to create synthetic zeolites made with specific channel dimensions for specific hydrocarbon mixes. Of the approximately 200 currently known zeolite minerals, at least 150 are synthetic (Ming and Mumpton, 1989).

Also related to the molecular seiving effect is the cation or molecular selectivity of zeolites.

Cation selectivity in clinoptilolite was first studied by Ames (1960), who discovered a strong preference for cesium in clinoptilolite. Since then, cation selectivities of many other zeolite minerals have been determined. These studies have shown that zeolites preferentially sorb heavy metals. Just as different zeolite minerals have different channel dimensions and thus have different molecular seiving properties, different zeolite minerals will preferentially sorb different heavy metals (Ming and Mumpton, 1989). Thus, specific zeolite minerals can be chosen for selective removal of the desired heavy metals. Indeed, clinoptilolite has been used to selectively remove radioactive cesium from nuclear reactor wastewater, and to remove ammonium from municipal wastewater streams (Ming and Mumpton, 1989). The molecular selectivity properties of zeolites have been used to remove nitrogen from oxygen, for example, since zeolites will preferentially sorb nitrogen in the presence of oxygen.

Zeolites have also been used as soil conditioners, as sorbents for odor control in animal manures and cat litter, as aquarium additives, and in a variety of other applications. In this project and other ongoing projects at New Mexico Tech and elsewhere, zeolites are currently being investigated for their potential use in sorbing various organic and inorganic forms of hazardous wastes.

Clinoptilolite Properties

Clinoptilolite is the most abundant naturally occurring zeolite (Ming and Dixon, 1988). A representative unit cell formula for clinoptilolite is $(Na_2,K_2,Ca)_3(Al_6Si_{30}O_{72})\cdot 24H_2O$ (Ming and Dixon, 1987a). The sodium, potassium, and calcium are all exchangable cations, and as such their relative proportions may vary, or they may be replaced completely by another cation, such as cesium or ammonium.

Clinoptilolite has a two-dimensional channel structure, consisting of an 8-ring channel parallel to a 10-ring channel in one dimension, that are both interconnected with another 8-ring channel running perpendicular to these. The cavity dimensions of these rings (in angstroms) are: 4.0 x 5.5, 4.4 x 7.2, and 4.1 x 4.7, respectively (Newsam, 1986). Thus the channels are not perfectly circular, but are actually polyhedral in nature (Barrer et al., 1967). The 10-ring opening is slightly larger than the 8-ring openings.

Zeolite Surface-Alteration

Barrer et al. (1967) conducted extensive studies on the exchange of organic cations with sodium ions in clinoptilolite. The organic cations they used included a variety of primary, secondary, tertiary, and quaternary ammonium cations. They found that the quaternary ammonium cations tetramethylammonium and tert-butylammonium were completely excluded from the internal zeolitic surfaces. Trimethylammonium, iso-propylammonium, and n-butylammonium cations were all partially exchanged within the zeolitic channels. Partial exchange may in some cases be explained by the molecular size of the exchanging cation. Although some organic cations may be able to enter all the zeolitic channels, the organic chains may fill all the zeolitic intracrystalline volume before complete replacement of all inorganic ions occurs. Thus only partial exchange is allowed. Primary and secondary ammonium cations with fewer than four carbons were all completely exchanged for sodium within the zeolite structure. The implication of Barrer's research is that quaternary ammonium cations are not effective at altering the internal zeolitic surface properties from hydrophilic to hydrophobic. The small channel openings effectively exclude any quaternary ammonium cations.

Some zeolite minerals, however, have large enough channel openings to allow the entry of quaternary ammonium cations. Offretite, for example, and many of the synthetic zeolites have channel openings large enough to allow the entry of TMA (Barrer, 1978). However, once the offretite mineral is saturated with TMA, this large cation effectively blocks channel openings so that even a relatively small molecule such as n-hexane was found to be excluded (Barrer, 1978). Normally, offretite saturated with metal cations will sorb both n-hexane and 2,2-dimethylbutane (Barrer, 1978). Although synthetic zeolites with larger openings are available, they were not investigated because most synthetic zeolites are less than 5 μm in diameter (Newsam, 1986), and would thus eliminate the advantage of large particle size.

Hydrophobic zeolite surfaces may be created by altering the zeolite mineral formula. It is well known that silica-rich zeolites (those with a high SiO_2:Al_2O_3 ratio) are less hydrophilic than those with a low SiO_2:Al_2O_3 ratio (Barrer, 1978). Zeolites with fewer Al^{3+} substitutions for Si^{4+} have a higher SiO_2:Al_2O_3 ratio and a lower charge density; and therefore the amount of essentially neutral mineral surface is higher than zeolites with lower SiO_2:Al_2O_3 ratios. As the amount of neutral surface area increases, the zeolite sorption capacity for hydrophobic compounds increases (Barrer, 1978). However, because all natural zeolites contain aluminum substitutions for silicon, all natural zeolites are inherently hydrophilic, although to different degrees. It has been shown that a combination of acid and heat treatments can extract structural aluminum from zeolites and create Si-O bonds at crystalline edges, thus resulting in a less hydrophilic zeolite surface that has almost no negative charge (Barrer, 1978; Chen, 1976). Excessive dealumination, however, can result in a structural rearrangement that actually decreased the sorption of some hydrophobic substances, presumably because the internal surface area was reduced (Chen, 1976). Although this method appears effective in creating less hydrophilic surfaces, it requires a very expensive and intricate experimental set-up, and the procedure must be conducted with extreme care to optimize the hydrophobic surface. As a result, this potential method for creating hydrophobic zeolite surfaces was not investigated further.

III.

MATERIALS AND METHODS

MATERIALS

Sorbent Selection

The clinoptilolite-dominated zeolite used was supplied by the Zeotech division of Leonard Minerals (Albuquerque, New Mexico), from their mine near Tilden, Texas. The material was seived to a gradation of grain sizes ranging from 0.2-2.0 mm. The sample was not a pure zeolite, but contained a significant percentage of smectite clay minerals. This combination of zeolites and clay minerals was an ideal mix for this study, providing a high CEC and suitable particle diameter. Quaternary ammonium cations could exchange on sites between clay lamellae and on external zeolite surface sites, thus creating an outer hydrophobic surface, with only the internal zeolitic channels remaining hydrophilic.

Surface-Modifying Agent Selection

Quaternary ammonium cations were selected as the surface altering agents for this project. As discussed in section II, the use of synthetic zeolites or aluminum extraction procedures for surface alteration were determined to be impractical for this project. The option of using a protonated amine (primary or secondary) to alter zeolite surface hydrophobicity was discarded since the protonated state of amines is dependant on solution pH, and in basic solutions the hydrophobic surface may be too easily degraded. In addition, the amines would have to have such short chains to fit into the internal zeolitic channels that their effect on external surface-alteration may not have been significant.

Several quaternary ammonium cations were evaluated for use as surface-altering agents. These were: TMA, phenyltrimethylammonium (PTMA), hexadecyltrimethylammonium (HDTMA), and methyl-4-phenylpyridinium (MPP). The first three cations were selected because they have been used by other researchers and have proven effective in altering clay hydrophobicity (Boyd et al., 1988b, 1988c; Cadena, 1988, 1989; Cadena and Jeffers, 1987; Jaynes et al., 1989; Mortland et al., 1986; and Smith et al., 1990). The last cation, MPP, was chosen specifically because pyridinium compounds have not been very well studied in the field of mineral surface alteration, and because this particular compound emphasized the phenyl functional group.

Both preliminary analyses of this project and research by others (Boyd et al., 1988c; Mortland et al., 1986) indicated that TMA and PTMA gave lower organic carbon contents than the larger organic cations (see App. E). In addition, TMA and PTMA may not fully cover the mineral surface, resulting in a mixed hydrophobic-hydrophilic surface that is generally not as effective at removing nonpolar organic contaminants from solution as larger organic cations. As a result, HDTMA and MPP cations were chosen as surface-modifying agents. These two cations have 19 and 12 carbons, respectively, so their effect on soil organic carbon content is significant. In addition, they emphasize the differences between the alkyl functional group and the phenyl functional group on surface alteration. HDTMA was supplied in liquid form as the chloride salt from Aldrich Chemical Co., (Milwaukee, Wisconsin). MPP is no longer commercially available, so it was synthesized in our lab. Details of the synthesis are provided in Appendix B.

Organic Solute and Solvent Selection

The organic solutes chosen for study were: phenol (Ph), ethylbenzene (Eben), tetrachloroethylene (PCE), and 1,1,1-trichloroethane (TCA). As shown in Table 2-1, these solutes have been used in relatively few studies of sorption to organo-clays, and thus are a new addition to the increasing literature database. In addition, each of these chemicals is listed on the U.S. Environmental Protection Agency's priority pollutant list, and is commonly found at industrial and hazardous waste sites (Keith and Telliard, 1979). Eben and Ph emphasize the phenyl functional group, with Ph a polar molecule (dipole moment, $\mu = 1.70$ debyes), and Eben an essentially nonpolar molecule ($\mu = 0.35$ debyes). PCE and TCA emphasize the alkyl structure, with TCA having a small dipole moment of 1.57 debyes and PCE a completely nonpolar molecule ($\mu = 0$; dipole moments from Wesson, 1948). Additional solute properties are compiled in Table 3-1.

Because most environmental investigations and cleanups involve fate and transport analyses of organics in water, water was an obvious solvent. Because it is a standard procedure for studies involving clay minerals, aqueous solutions were made of distilled water with calcium chloride added to make a 0.005 M solution.

Table 3-1. Organic Solute Properties.

Solute	Molec. Weight	Density [mg/L][1]	Aq. Sol. [mg/L] (25°C)	Sat. Vap. Pres. [mm Hg] (temp.°C)[2]	Calculated K_H [−][a]	Log K_{ow}	Log K_{oc} (Log K_{om})
Eben	111.21	0.867	152[2]	7 (20)	2.76×10^{-1}	3.15[3]	(1.98)[4]
				12 (30)	4.72×10^{-1}	3.15[4]	
Ph	94.11	1.071	86600[5]	0.2 (20)	1.17×10^{-5}	1.46[6]	(1.48)[6]
		(solid)		1 (40)	5.85×10^{-5}	1.65 ± 0.19[7]	
TCA	133.41	1.338	1334[8]	100 (20)	5.38×10^{-1}	2.47[8]	2.25[9]
				155 (30)	8.34×10^{-1}	2.30[10]	
PCE	165.83	1.623	150[2]	14 (20)	8.33×10^{-1}	2.6[11]	2.81[12]
				24 (30)	1.43	2.53[8]	2.56[9]
						2.60[13]	2.60[10]

a = K_H (Henry's Constant) calculated as saturated vapor pressure over aqueous solubility, then converted to dimensionless units.
1 = Aldrich Chemical Co., 1990
2 = Verschueren, 1983
3 = Leo et al., 1971
4 = Chiou et al., 1983
5 = Stephen and Stephen, 1963
6 = Briggs, 1981
7 = Average of 35 values reported in Leo et al., 1971, with Standard Deviation
8 = Banerjee et al., 1980
9 = Karickhoff, 1981
10 = Hasset et al., 1980
11 = Boyd et al., 1988a
12 = Average of 2 values determined by Boyd et al., 1988a
13 = Chiou et al., 1977

However, some organic releases may involve large volumes of free organic liquid containing other dissolved organic solutes. In these instances, sorption of the organic solutes may behave quite differently from when the solutes are dissolved in water. Therefore, the sorption of these solutes from organic solvents was also determined. To evaluate the effects of contrasting properties, both polar and nonpolar organic solvents were desirable. Methanol was chosen as the polar solvent, and benzene as the nonpolar solvent. All the organic solutes were obtained from Aldrich Chemical Co.; benzene and methanol were obtained from Fisher Scientific (Pittsburgh, Pennsylvania). HPLC-grade methanol and thiophene-free benzene were used, while solutes were the highest purity available (99-99.9%). All compounds were used as-received from the supplier.

METHODS

Characterization of Porous Medium

Prior to conducting sorption experiments, the zeolite sorbent was characterized. The zeolite was characterized using x-ray diffraction (XRD), CEC analyses, and scanning electron microscopy (SEM). Although the material had been seived to a sand-sized fraction, preliminary experiments showed that some of the zeolite aggregates would break down with mechanical agitation into clay-sized particles. As a result, a sample was submitted to the New Mexico Bureau of Mines for XRD analysis of both the bulk mineral fraction and of the $<2\mu m$ fraction.

Because the literature indicated that the organic cations would only be exchanged on the external zeolite surfaces, it was important to characterize not only the total zeolite CEC, but also to determine the external CEC. Total CEC was determined by the method of Rhoades (1982), and internal and external CEC was determined by the method of Ming and Dixon (1987b). Detailed descriptions of these analytical methods and the procedures used are presented in Appendix C.

To characterize the zeolite surface morphology, the sample was submitted to the New Mexico Institute of Mining and Technology Materials and Metallurgy Department for SEM photography.

Quantification of Surface Modification

A procedure was developed to modify the zeolite surfaces using the large organic cations HDTMA and MPP. Several different zeolite:solution ratios and solution concentrations were investigated, along with the time necessary for complete exchange. The best method for surface modification was determined on the basis of simplicity and effectiveness in altering the surface. The method ultimately chosen to create the modified surfaces was essentially to add an amount of organic cation equal to the external CEC, equilibrate 24 hours, then rinse and dry the treated zeolite. This method is presented in detail in Appendix D.

Once the modified surface had been created, it was necessary to quantify the extent of surface modification so that comparisons could be made between differently treated surfaces. Two different methods were used for this purpose: sorption isotherms of each organic cation were developed, and the organic carbon content of the resultant treated zeolite was measured.

Sorption isotherms were generated using a ^{14}C radiolabelled organic cation. Methyl-labelled HDTMA and MPP cations were supplied by American Radiolabelled Chemicals, Inc., (Saint Louis, Missouri). A radioactive spike of the appropriate cation was added to each of several solutions of different concentrations. The solutions were added to the zeolite and equilibrated for 24 hours, following the treatment procedure outlined in Appendix D. A 1-mL aliquot of equilibrated and centrifuged solution was withdrawn from each sample and added to a 20-mL glass scintillation vial. Ten mL of Ecolite scintillation cocktail (ICN Biochemicals, Inc., Irvine, California) was added to each sample. All samples were stored at 5°C overnight before analysis in a Tri-Carb 460CD liquid scintillation system (Packard Instrument Co., Inc., Downer's Grove, Illinois). MPP samples were corrected for quenching using a quench curve generated from MPP standards.

Organic carbon content was measured using a carbon oxidation method conducted in a sealed ampule, after which CO_2 generated was quantified. Detailed analytical steps are outlined in Appendix E. The organic carbon analyzer (O.I. Corp., College Station, Texas) consisted of Model 524 P.S. purging and sealing unit, Model 524 D ampule analyzing unit, and Model 3300 IR gas analyzer.

Quantification of Modified Surface Stability

Once the modified surface had been successfully created and quantified, it was necessary to confirm that the modified surface would remain stable in the solutions in which studies would be conducted. Because the studies in this project were all batch studies of 72 hours or less in duration, the stability over 72 hours, under conditions identical to those of the studies to be conducted, was assessed. Long-term stability studies were not conducted.

Surface stability was assessed in a variety of aqueous and organic solutions, and in a range of pH buffers. Solutions in which surface stability was studied are shown in Table 3-2. The calcium

Table 3-2. Solutions for Surface Stability Characterization.

0.005 M $CaCl_2$
0.01, 0.1, and 1.0 M CsCl
0.1 and 1.0 M phenyltrimethylammonium chloride (PTMA)
0.1 and 1.0 M tetramethylammonium chloride (TMA)
0.15 M HDTMA (to MPP-zeolite only)
0.15 M MPP (to HDTMA-zeolite only)
0.05 M Potassium hydrogen phthalate-0.02 M HCl pH 3.02 buffer
0.05 M KH_2PO_4-0.03 M NaOH pH 6.95 buffer
0.0125 M $Na_2B_4O_7 \cdot 10H_2O$-0.02 M HCl pH 8.12 buffer
0.025 M $NaHCO_3$-0.01 M NaOH pH 9.85 buffer
Distilled water
Soltrol
Methanol
Benzene

chloride solution was chosen because all the aqueous isotherms were to be conducted in 0.005 M $CaCl_2$ solution. The cesium chloride solutions were chosen because clays and zeolites have a high specificity for cesium sorption. Organic cation desorption in cesium solutions was considered to be a worst-case condition for replacement by inorganic cations. Buffers were used to evaluate surface stability over a range of pHs. In addition, these pH buffers contain high concentrations of sodium or potassium ions which may potentially exchange for the organic cations. Distilled water was evaluated because it was the solution used for rinsing the zeolites immediately after they had been treated. Methanol and benzene were chosen because they were the two organic solvents evaluated in the sorption isotherm experiments. Soltrol (a mixture a C_8 to C_{13} hydrocarbons) was chosen as an additional organic mixture because it is a commonly used organic mix in our labs to study oil entrapment in porous media. The organic cations were chosen to evaluate the strength of other large organic cations in displacing the modified-surface cations. A cation concentration of 0.15 M was equal to the external zeolite CEC at the zeolite mass and liquid volume used for these studies. All salt solutions were added at one concentration below the CEC equivalent concentration, and at one concentration above the CEC equivalent concentration. Specific concentrations, however, were arbitrarily selected.

These studies were conducted by treating a large mass of zeolite with ^{14}C labelled organic cation. After exchange, the supernatent ^{14}C concentration was measured, the zeolite was rinsed and dried, and ^{14}C concentration in the rinsate was measured. Based on the initial amount of ^{14}C labelled cation added to the zeolite, the treated zeolite activity was calculated. Five grams of the radioactively labelled MPP- or HDTMA-zeolite was mixed with 10 mL of each solution listed in Table 3-2. These mixes were sampled after 4, 8, 24, 48, and 72 hours to analyze the organic cation desorption over a span of a typical batch study. Supernatent solutions were analyzed using liquid scintillation in the same manner as was done for the cation sorption isotherms.

Quantification of Organic Solute Sorption to Modified Zeolites

Batch sorption studies were conducted to quantify the extent of organic solute sorption to each of the modified zeolites from the different solvents. For comparison, and to evaluate the effectiveness of internal zeolitic channel sorption sites, sorption studies to the natural (untreated) zeolite were also conducted. Prior to obtaining results of the sorption studies, an assessment of equilibrium time was performed. For this assessment, an intermediate concentration of each solute in each solvent was chosen and mixed with each zeolite. The solution concentrations were measured at 4, 8, 24, 48, and 72 hour intervals, to determine the equilibration time. Once the equilibrium time was established, the full suite of solution concentrations was prepared, and the complete isotherm was run.

Isotherm equilibrati times varied from 4-48 hrs
— see App. tables

Two different techniques were used to generate the sorption isotherms. The method used was dependant on the solute's volatility, as estimated from its Henry's Constant (K_H), as shown in Table 3-1. Phenol, which has a very low Henry's constant, was studied differently from the method used for Eben, PCE, and TCA, which have very high Henry's constants. All studies, however, were conducted in duplicate, with tube blanks carried throughout and treated exactly as any other samples, to determine loss due to volatilization or tube sorption.

For HDTMA zeolite, equil times:
Eben 8hr
PCE 4hr
TCA 4hr
phenol 24

Phenol sorption isotherms were generated using ^{14}C universally-labelled Ph (American Radiolabelled Chemicals, Inc.). Several Ph solutions ranging from 100-50,000 mg/L in each solvent were prepared, and spiked with the radiolabelled phenol. The solution was added to each different zeolite in a ratio of 2:1, respectively, with 5.0 mL solution pipetted into 50 mL, screw-cap (Oak Ridge-type) teflon centrifuge tubes containing 2.50 g zeolite. The mixture was equilibrated, centrifuged, and 1.0 mL supernatent removed and placed into 20 mL glass scintillation vials. Ecolite scintillation cocktail was added to each vial in a ratio of 10 mL cocktail:1 mL sample. Samples and standards were then analyzed via liquid scintillation. Since quenching was not observed, no correction for quenching was added. Since Ph recovery in blank samples (containing no zeolite) was never less than 97%, no correction for blanks was made.

The remaining three solutes required special care due to their volatility. For these isotherms, solutions were prepared in 125 mL Wheaton (Millville, New Jersey) crimp-top bottles at different concentrations, ranging from approximately 10 mg/L to 100 mg/L. Bottles were capped with teflon-lined butyl rubber septa. Solution was withdrawn using a 100 mL gas-tight syringe. From this syringe, solution was added to 10 mL Wheaton crimp-top vials containing 2.50 g zeolite. These vials had already been sealed with teflon-lined silicone septa, so the solution was added by piercing the septa and injecting solution until the vial was filled. To permit maximum filling of the vials with solution, a vent needle was pierced through the septum to allow gas in the vial to escape. Even with the vent needle, however, vials could not be completely filled with solution. The headspace volume remaining in each vial, however, was negligible relative to the total vial volume, and was highly reproducible.

Following solution addition, samples were equilibrated, centrifuged, and 2.0 mL supernatent was withdrawn by piercing the septum again with the gas-tight syringe and placed in 2.0 mL gas chromatograph (GC) autosampler analysis vials. Blank vials, containing no zeolite, were prepared, equilibrated, and sampled identically to the zeolite-containing samples. All solutions were analyzed with a Hewlett Packard (Palo Alto, California) Model 5890 GC equipped with a flame-ionization detector and Model 3396A integrator. Concentrations in the blank samples after equilibration were considered to be the initial solution concentration for isotherm calculations. Gas flow rates for all solute-solvent combinations except for TCA in benzene were the same, as shown in Table 3-3. Because TCA and benzene could not be separated with the column used for all other analyses, a separate column and gas flow rates were used for these analyses, as shown in Table 3-4. GC settings were slightly different for each of the compounds, and these are shown in Table 3-5. With the parameters used as described in Tables 3-3 and 3-4, and 3-5, typical compound retention times and detection limits, respectively, are: Eben, 1.64 min., 0.3 mg/L; PCE, 1.35 min., 0.7 mg/L; TCA, 1.81 min, 0.3 mg/L; TCA in benzene, 5.92 min., 0.3 mg/L. With the parameters used, the minimum peak area that could be detected was typically about 50 integrator units. Detection limits were determined as a peak area of 70 divided by an average peak area for a 200 mg/L standard. Analyses of solute concentrations over this range indicated linear calibration curves. Parameters that serve only to improve the chromatogram appearance, such as chart speed, attenuation, and other report options are not included in the tables. Data were analyzed as peak areas and compared to known standards at 200 mg/L concentration in methanol as supplied by Supelco, Inc. (Bellefonte, Pennsylvania). TCA in benzene concentrations were determined from a standard curve prepared in our lab over a range of TCA concentrations. The measured standard curve was linear and is presented as Figure 3-1. Eben sorption from benzene was not characterized due to an Eben impurity in the benzene solvent used.

Table 3-3. Gas Chromatrograph Equipment and Gas Flow Rates. For Analysis of Eben and PCE in water, methanol, and benzene; and TCA in water and methanol.

Gas Chromatograph Model:	HP 5890
Detector:	Flame Ionization
Column:	HP-5 (5% Phenyl Methylsilicone) (Hewlett Packard, Palo Alto, CA) 10 m 0.53 mm ID
Carrier Gas:	He, 5.7 ml/min.
Make-up Gas:	N_2, 30 ml/min.
Air:	420 ml/min.
Hydrogen:	35 ml/min.
Septum Purge:	3.12 ml/min.
Split Vent:	5.65 ml/min.

Table 3-4. Gas Chromatrograph Equipment and Gas Flow Rates. For Analysis of TCA in Benzene.

Gas Chromatograph Model:	HP 5890
Detector:	Flame Ionization
Column:	Econocap Carbowax (Alltech Assoc., Deerfield, IL) 30 m 0.53 mm ID
Carrier Gas:	He, 3.02 ml/min.
Make-up Gas:	N_2, 28.3 ml/min.
Air:	390 ml/min.
Hydrogen:	30.0 ml/min.
Septum Purge:	1.72 ml/min.
Split Vent:	5.31 ml/min.

Table 3-5. Gas Chromatograph and Integrator Settings.

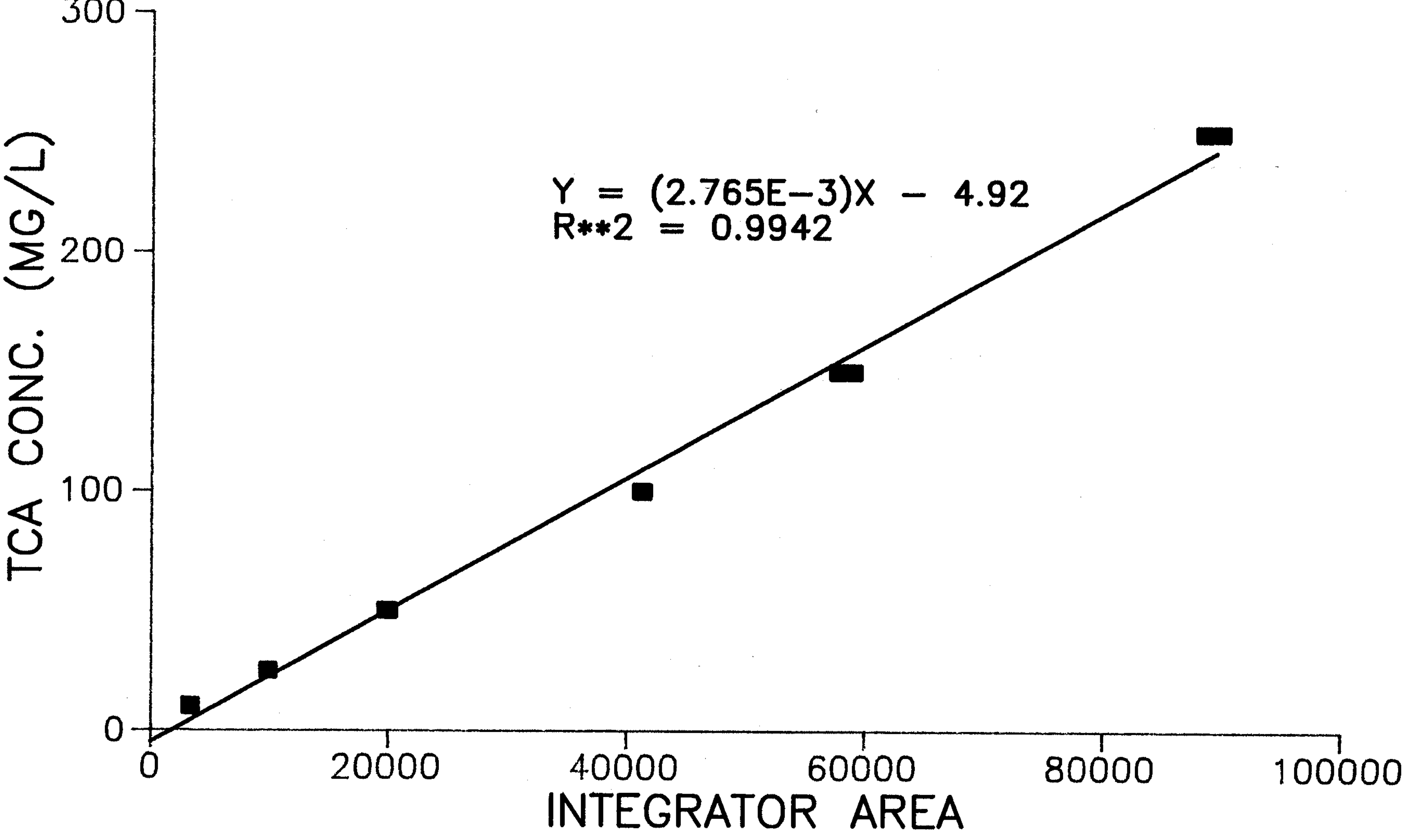
Setting	Organic Solute Eben & PCE	TCA
Threshold	-2	-4
Peak Width	0.04	0.06 0.09^b
Zero	0	0
Area Rej.	0	0
Initial Oven Temp. (°C)	100	40 70^b
Injector Temp. (°C)	200	200 250^b
Detector Temp. (°C)	250	250 275^b
Purge A	On	On
Purge B	On	On

Notes: Samples in Aqueous solution were run with an oven profile starting at the given initial temperature and ramping to 150°C at 10°/min. Samples in benzene and methanol

were run isothermally.

b = Parameters for TCA analysis in benzene.

FIGURE 3—1.
TCA STANDARDS IN BENZENE



IV.

RESULTS AND DISCUSSION

POROUS MEDIUM CHARACTERIZATION

XRD and SEM Results

Sample mineralogical data provided by Leonard Minerals indicated that the zeolite sample mineralogy was approximately 60% clinoptilolite, 20% montmorillonite, 15% amorphous material, and the remainder carbonates and other materials. The Bureau of Mines XRD analysis of the bulk sample confirmed this analysis, although the amorphous materials were not well identified on the XRD output. Dr. Doug Ming, currently of NASA, has extensively studied the Tilden deposit and other zeolites, and has found that acid pretreatments such as the one we used to remove carbonates (see Appendix D) will often mask the presence of amorphous materials (personal communication, 1989). Analysis of the $<2\mu$m fraction, however, indicated this particle range was primarily smectite minerals (~80%), with the remainder clinoptilolite. Ming (1989, personal communication) has conducted XRD analyses on a range of sizes of the Tilden clinoptilolite, and confirms that the smaller particle sizes are predominantly smectite minerals, while the larger particle sizes contain higher percentages of clinoptilolite.

Scanning electron microscope photography failed to reveal crystalline zeolitic surfaces, as shown in Fig. 4-1. The material appears to be mineral aggregates of zeolite cemented with smectite minerals and amorphous materials.

It was noticed during the course of the research that these zeolite aggregates often mechanically broke down into smaller particles upon agitation. Apparently, some of the clay minerals are poorly cemented to the aggregates, and can be dislodged when the material is shaken for a prolonged period of time ($>$24 hours). In addition, treatment with HDTMA cations resulted in a finer particle size than initially added. It is theorized that the HDTMA cations enter into the interlamellar spaces of the smectites, and upon sorption force the layers apart. A corresponding widening of layer spacing has been documented by other researchers doing XRD analyses of treated clay minerals (Cowan and White, 1962). As the cations can force apart clay layers of a single mineral, these cations may also force apart adjacent clay plates, inducing a dispersing effect, and thus resulting in a smaller particle size. This dispersing effect appears to be pimarily mechanical in

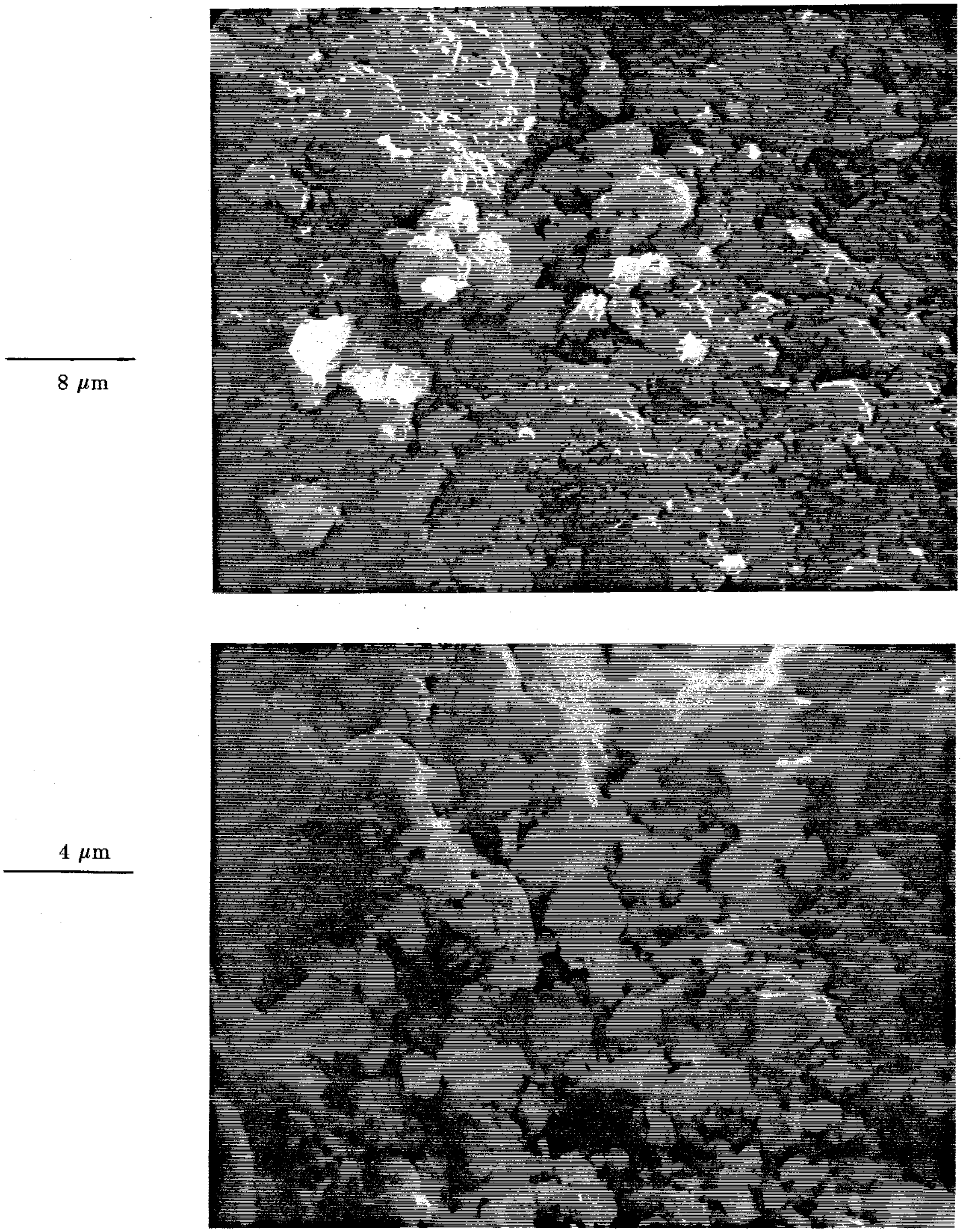


Figure 4-1. SEM Photographs of Zeolite Surfaces.

nature; that is, the mineral chemistry is not changed except that the surface is saturated with organic rather than inorganic cations, so the resulting smaller particle size does not change the sample characteristics. The exchange of the organic cation may, however, result in an increased available surface area for sorption.

CEC Results

Results of the bulk sample CEC indicated a total CEC of approximately 60 me/100 g, an internal CEC (zeolitic internal channels) of approximately 30 me/100 g, and an external CEC (smectite CEC and external zeolite surface CEC) of approximately 30 me/100 g. The complete data and results calculations are presented in Appendix C. These values are significantly lower than the CEC's reported by others for different subsamples of the Tilden zeolite. The Leonard Minerals data indicated a total CEC of approximately 160 me/100 g. Data from Ming (1989, personal communication) indicated a CEC of 90-120 me/100 g, and data from Haggerty (1990, personal communication) indicated a total CEC of approximately 40 me/100 g.

These differences may be explained in part by differences in CEC measurement methodology. Methods used for this research and by Haggerty followed those of Rhoades (1982). This method is essentially a sodium saturation of exchange sites, followed by sodium replacement by magnesium. The method used by Leonard Minerals was an ammonium acetate exchange, whereby exchange sites were saturated with sodium, followed by replacement with ammonium. This method may often result in an overestimate of CEC, especially in zeolitic minerals, where ammonium may extract nonexchangeable sodium from the zeolite structure (Polemio and Rhoades, 1977). Conversely, an exchange of magnesium for sodium, as is done in the Rhoades method, may result in an underestimate of CEC, since sodium is greatly preferred by clinoptilolite over magnesium (Ming and Mumpton, 1989), and therefore Mg exchange for Na may be incomplete. In addition, sodium saturation of exchange sites may be incomplete, since some common exchangable cations, particularly potassium and calcium, are greatly preferred over sodium (Ming and Dixon, 1987a). The method used by Ming was a potassium/cesium exchange, whereby exchange sites were saturated with potassium, then replaced with cesium. This method should be very accurate, since both potassium and cesium are strongly preferred by clinoptilolite (Ming and Dixon, 1987a).

Although these differences in CEC measurement methodology may contribute to small errors in sample CECs, it is not likely that more than a factor of four (40-160 me/100g) is due to simple method variations. More likely is that the mineralogy of the deposit varies spatially, and the sample location will affect its mineralogical and thus CEC properties. This is further supported by the fact that in this study, two different methods were used to determine CEC, one for the total CEC and one for the internal and external CEC. Both these methods gave comparable results (see Appendix C). Haggerty (1990, personal communication) also measured an external CEC of approximately 30 me/100g, so it is likely that the amount of smectites is relatively constant across the sample deposit, while the amount of amorphous materials and clinoptilolite may vary spatially. As the amount of amorphous material decreases and the clinoptilolite content increases, the total CEC will increase, since amorphous materials contribute little, if at all, to the sample CEC. Conversely, as the clinoptilolite content decreases and the amorphous mineral content increases, the sample total CEC will decrease. However, with the clay mineral content remaining approximately constant, the external CEC will be relatively constant.

QUANTIFICATION OF SURFACE MODIFICATION

Organic Cation Sorption isotherms

Sorption isotherms for HDTMA and MPP exchange to the zeolite are presented as Fig. 4-2 and 4-3, respectively. These isotherms are classical Type H isotherms, indicating the sorbent has a strong preference for the sorbate up to a certain point, after which point the sorption capacity is essentially satisfied and sorption decreases significantly or ceases (Giles et al., 1974). In these cases the point at which sorption begins to decrease is very near the sorbent's external CEC. At concentrations beyond the external CEC, the figures clearly show that HDTMA is much more strongly sorbed than MPP, but that sorption continues to as much as 2.5 times the external CEC for MPP and up to 7.5 times the external CEC for HDTMA. Duplicate agreement was poor at very high cation concentrations. The complete data results, including quenching corrections, are presented in

FIGURE 4—2. HDTMA SORPTION TO ZEOLITE
CEC IS SATISFIED AT 85,465 MG/KG

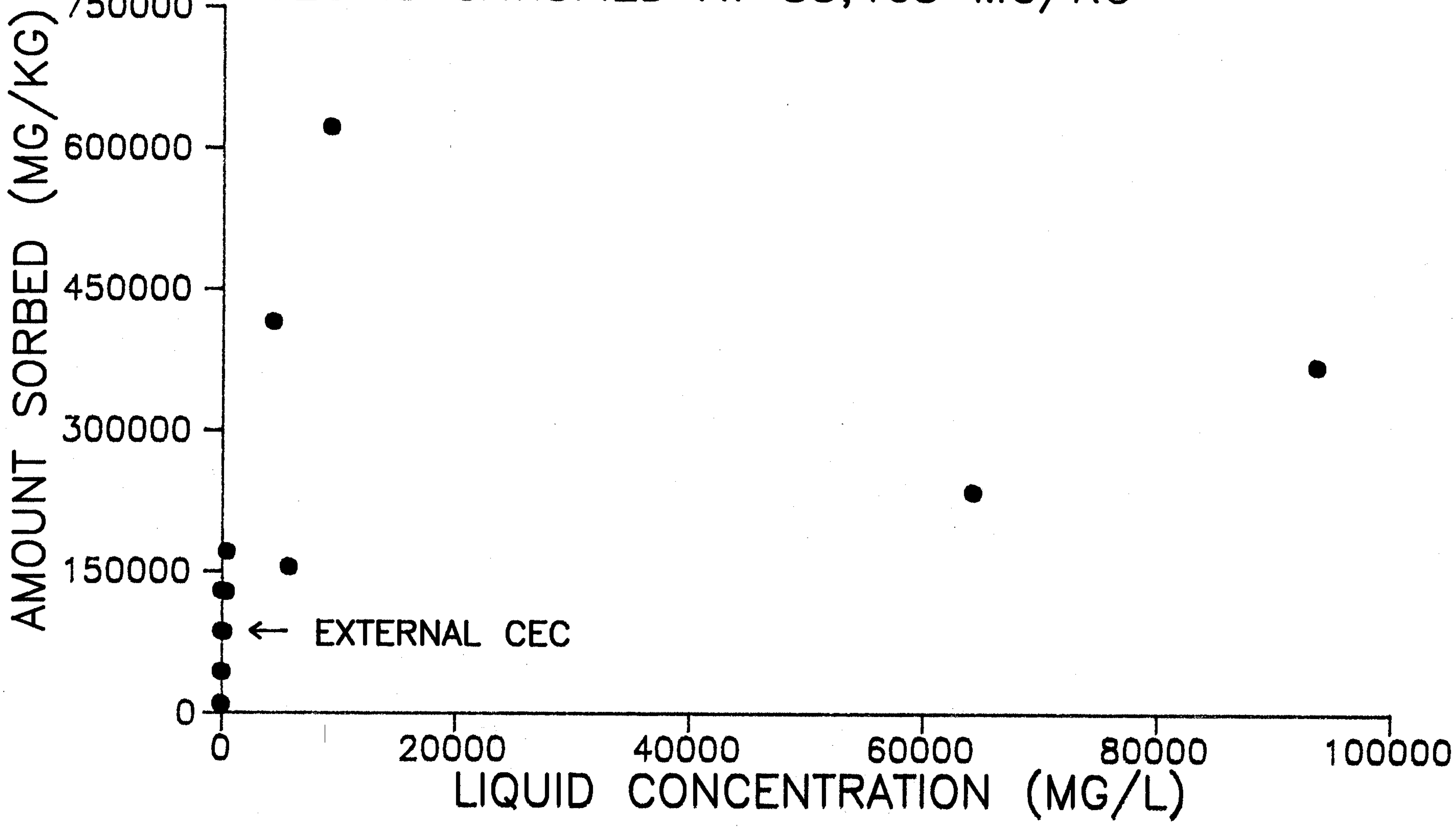
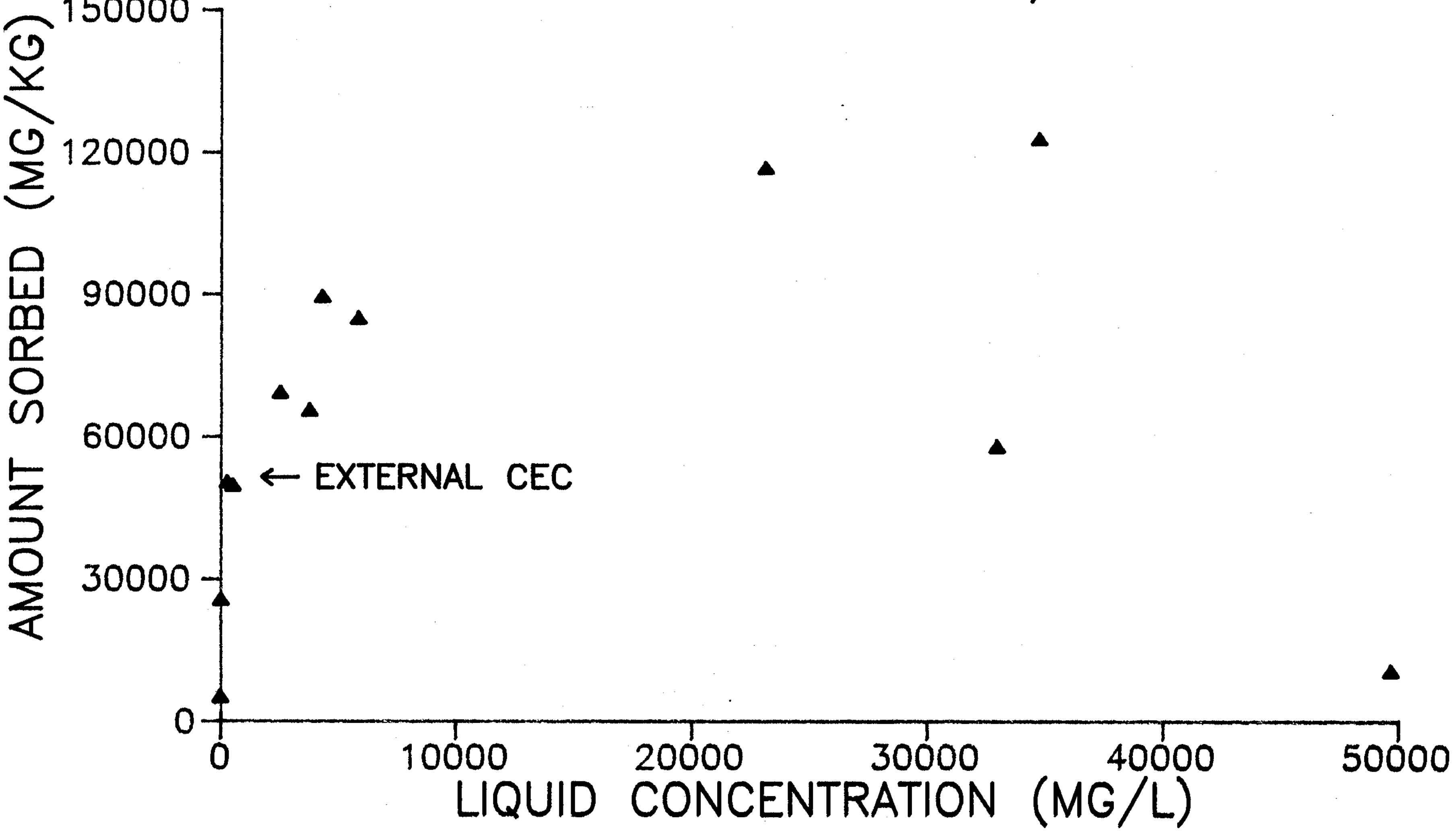


Figure 4—3. MPP SORPTION TO ZEOLITE
CEC IS SATISFIED AT 51,123 MG/KG



Appendix F.

The poor duplicate agreement may be due in part to the type of bonding that occurs at concentrations greater than the sample CEC. At organic cation concentrations above the CEC, hydrophobic tails of the large cations in solution may sorb to the hydrophobic ends of cations already bound to the mineral surface. Some researchers have referred to this type of bonding as "hydrophobic bonding" (Hamaker and Thompson, 1972; Mortland, 1986), whereby the hydrophobic tails of organic molecules associate with each other as a result of both weak Van der Waals forces between organic chains and an entropy driven effect, as discussed in section II. However, in the case of organic cations, perhaps a more accurate term describing the type of bonding that occurs is "amphipathic adsorption" (Black, 1969). An amphipathic molecule is one having both a polar and nonpolar functional group. In the case of these large organic cations, the polar group is the charged quaternary ammonium end, and the nonpolar group is the long organic chain. Amphipathic adsorption occurs when the long hydrophobic tail is oriented away from the water and towards the mineral surface, with the polar group oriented towards the water.

Thus, two completely different sorption mechanisms operate, depending on whether the organic cation concentration is above or below the sorbent's CEC. At cation concentrations below the CEC, sorption is via cation-exchange. The large cation simply replaces the smaller inorganic cations saturating suface exchange sites, oriented with the positive end towards the mineral surface, to satisfy the surface charge imbalance. This type of sorption results in an ionically balanced mineral surface that has long organic chains extending out into the solution, and thus imparting hydrophobic properties to the surface.

As discussed in section II, both enthalpy and entropy favor the sorption of large organic cations over small inorganic cations, and the data show that both HDTMA and MPP were quantitatively sorbed up to the sorbent CEC. The isotherm data (Appendix F) show that when an amount of organic cation equal to the zeolite CEC was added to the zeolite, over 98% of HDTMA was sorbed, and over 95% of MPP was sorbed.

Once the CEC is met, molecules can no longer orient themselves with the positive end towards the mineral surface, because there is no counterbalancing negative charge to maintain the charge balance. However, amphipathic adsorption does take place, presumably entropy driven by the disintegration of the rigid water structure surrounding the hydrophobic tails. In this case, the molecule orientation is reversed. The hydrophobic tails orient themselves towards the mineral surface, which is saturated with other hydrophobic tails, and the positive quaternary ammonium cation is oriented towards the solution. If the surface-saturating hydrophobic tails create an essentially continuous organic medium, the amphipathic sorption may more nearly behave as a partitioning. However, because this type of partitioning is not necessarily exothermic, and may be only weakly favorable thermodynamically (Chiou et al., 1979), it may not necessarily occur consistently and reproducibly. In addition, steric hinderences of these large organic cations, which, once sorbed, block off other potential amphipathic adsorption sites, may contribute to the poorly reproducible nature of high concentration sorption. In any case, these sorption isotherms show that the organic cations are quantitatively sorbed at concentrations up to the CEC, and that sorption can occur at concentrations well above the sorbent CEC.

Organic Carbon Content

The second method used to quantify the extent of surface modification was via organic carbon content on the modified zeolite. A complete explanation of methods used and raw data is presented in Appendix E. The results showed that HDTMA zeolite had an organic carbon content of 6.33% (by weight), and MPP zeolite had an organic carbon content of 3.80%. A comparison of these results to the theoretical zeolite organic carbon content at 100% organic cation exchange efficiency showed 99.7% and 91.8% exchange efficiency of HDTMA and MPP ions, respectively. The values disagree slightly with the values determined from the sorption isotherms primarily because of the different methods employed for each of the carbon loading determinations (^{14}C vs. carbon oxidation). Nonetheless, the organic carbon analysis confirmed that the organic carbon increased significantly over the untreated zeolite, which had a measured organic carbon content of 0.16% (see Appendix E).

QUANTIFICATION OF MODIFIED SURFACE STABILITY

Equilibrium desorption of the surface-altering organic cation was reached in almost every case after four hours, the shortest time increment evaluated. Figure 4-4 is representative of the pattern shown by the HDTMA and MPP zeolites in essentially all of the solutions evaluated. The figure shows equilibrium was reached within four hours, slightly more MPP desorption than HDTMA desorption, and excellent duplicate agreement (duplicate points at each time are plotted). Complete data results are presented in Table 4-1. The result shown is the average of all duplicates after equilibrium was reached.

Table 4-1.
Surface Stability Results.

Solution	% Remaining HDTMA	% Remaining MPP
pH 3.02	99.67	97.33
pH 6.95	99.62	98.59
pH 8.12	99.61	98.44
pH 9.85	99.56	98.97
Distilled Water	99.51	99.47
0.01 N $CaCl_2$	99.56	98.96
0.01 M CsCl	99.57	98.97
0.1 M CsCl	99.59	96.96
1.0 M CsCl	99.14	90.44
Benzene	99.83	99.93 (bkgnd)
Soltrol	99.93 (bkgnd)	99.95 (bkgnd)
Methanol	91.23	99.75
0.1 M TMA	98.87	94.17
1.0 M TMA	97.68	85.72
0.1 M PTMA	99.31	98.31
1.0 M PTMA	67.96	68.66
0.15 M HDTMA	---	76.60
0.15 M MPP	98.73	---

The results in Table 4-1 show that the HDTMA zeolite was stable over a range of pH's, in all the inorganic salt solutions, in benzene, and in soltrol, with over 99% of the original HDTMA loading retained on the zeolite after equilibrium. In methanol, however, almost 9% of the HDTMA was removed. The reasons for this are unclear at this time; however, this experiment was repeated with nearly identical results, so it is unlikely that experimental error was to blame. This result is

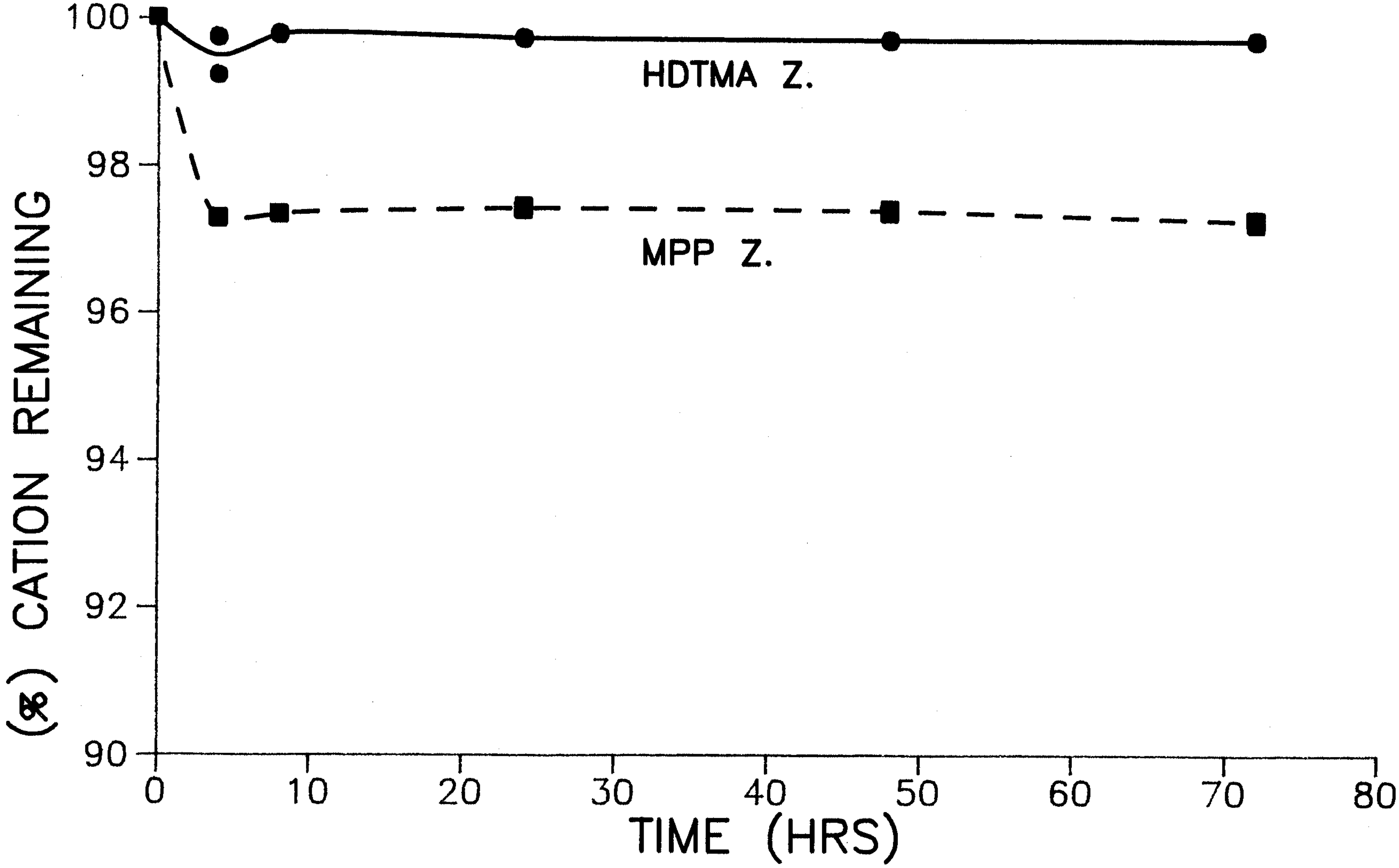


FIGURE 4—4. ORGANIC CATION DESORPTION.
pH 3.02 SOLUTION

consistent with results found by Jordan (1963), as discussed in section II. As Jordan proposed, this amount of desorption may represent only weakly amphipathically bonded HDTMA, rather than an actual desorption of surface-exchanged ions.

In the organic salt solutions, TMA caused only a small amount of HDTMA desorption, and only very high concentrations of PTMA caused a significant amount of HDTMA desorption. MPP was not very effective at competing with HDTMA for surface sorption sites once the HDTMA ion was sorbed.

Comparison of MPP desorption in the same solutions showed that in general, approximately one half- to one percent more MPP cations than HDTMA ions were removed at equilibrium. This indicates that MPP was not quite as strongly bound to the zeolite surface as HDTMA was. There are some minor differences in the desorption behaviour of the two suface-altering agents. For instance, essentially no MPP was removed in methanol. However, MPP was removed by almost 10% in the most concentrated cesium chloride solution. Recall that at the zeolite mass and solution volume used, a concentration of 0.15 moles/L of charge was equivalent to the external CEC. Therefore, an amount of cesium in large excess of the CEC was required to affect a 10% desorption of MPP. Similar trends were seen with the other organic cations. While MPP replacement by PTMA was essentially the same as that for HDTMA, high concentrations of TMA were somewhat more effective at replacing MPP than HDTMA. In addition, HDTMA was effective at replacing almost 25% of the sorbed MPP ions.

In summary, these data showed that equilibrium desorption of sorbed organic cations was reached within a few hours. HDTMA was slightly more strongly sorbed than MPP ions; however, generally an extreme excess of cations over the external CEC was required to affect as much as a 10% removal of the originally sorbed organic cation. Other large organic cations, however, were slightly more effective than inorganic cations at replacing the sorbed organic cations, especially at the high concentrations. In general, these data support the thermodynamic theory presented in section II. The relatively high desorption of HDTMA in methanol cannot be fully explained at this time.

QUANTIFICATION OF ORGANIC SOLUTE SORPTION TO MODIFIED ZEOLITES

Organic solute sorption isotherms are presented for each zeolite-solvent combination in Fig. 4-5 to 4-20. Each set of figures for a single solute was plotted on the same scale to facilitate rapid visual comparisons. A quick assessment of basic isotherm shapes and characteristics reveals several general trends. Phenol isotherms were nonlinear, and covered a much larger concentration range than Eben, PCE, or TCA. The latter three solutes all showed very linear sorption isotherms. While Ph was slightly sorbed from benzene and methanol, the other solutes are not sorbed at all from the organic solvents.

These differences in sorption isotherm shapes can be explained largely in terms of different properties between Ph and the other solutes. Specifically, the hydroxyl group of Ph imparts several specific properties absent in the other compounds. The hydroxyl group not only contributes to the strong dipole moment of Ph, but also allows the molecule to enter into hydrogen-bonding type of interactions. While TCA has a dipole moment approaching that of Ph (1.57 vs. 1.70 debyes, respectively), TCA has little propensity for hydrogen bonding interactions. Eben and PCE are both essentially nonpolar, so they will not enter into hydrogen bonding associations or ion-dipole type interactions. Because of the Ph hydroxyl group and the accompanying hydrogen bonding, Ph is much more soluble in aqueous solutions than the other molecules, and therefore the range of solution concentrations evaluated for Ph spanned two and a half orders of magnitude more than all the other solutes. Because of these differences in properties, solubility, concentration range evaluated, and isotherm shape, the following discussion of results will be divided into two parts: the first describing results specifically of Ph sorption, and the second analyzing the three remaining solutes as a similar group.

Phenol Sorption Assessment

Phenol Sorption from Aqueous Solution

The sorption isotherms show that HDTMA-zeolite was the most effective Ph sorbent from aqueous solution (Fig. 4-8). When these data were analyzed on the basis of organic carbon mass,

FIGURE 4—5.
PHENOL SORPTION TO HDTMA ZEOLITE

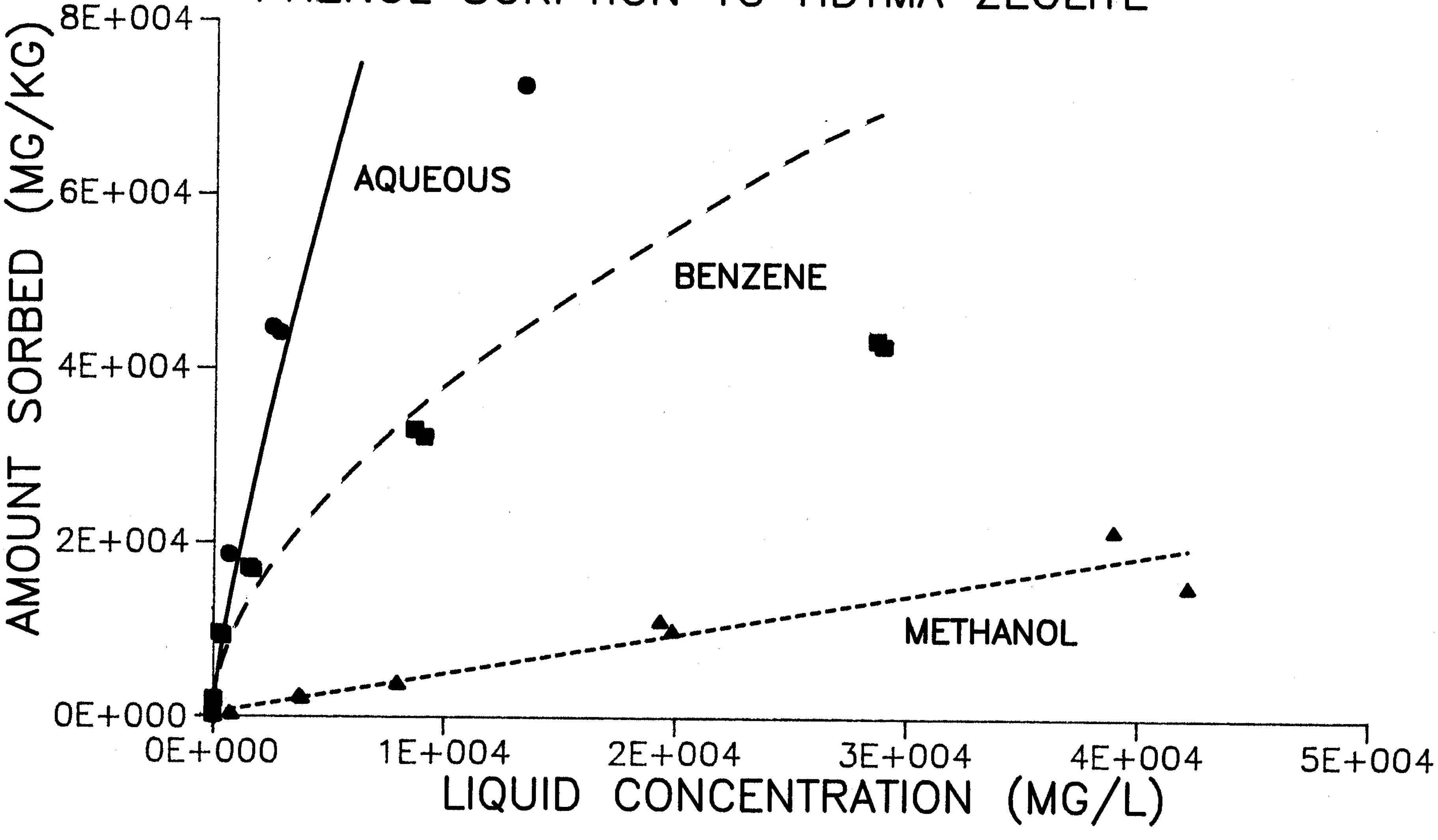


FIGURE 4–6.
PHENOL SORPTION TO MPP ZEOLITE

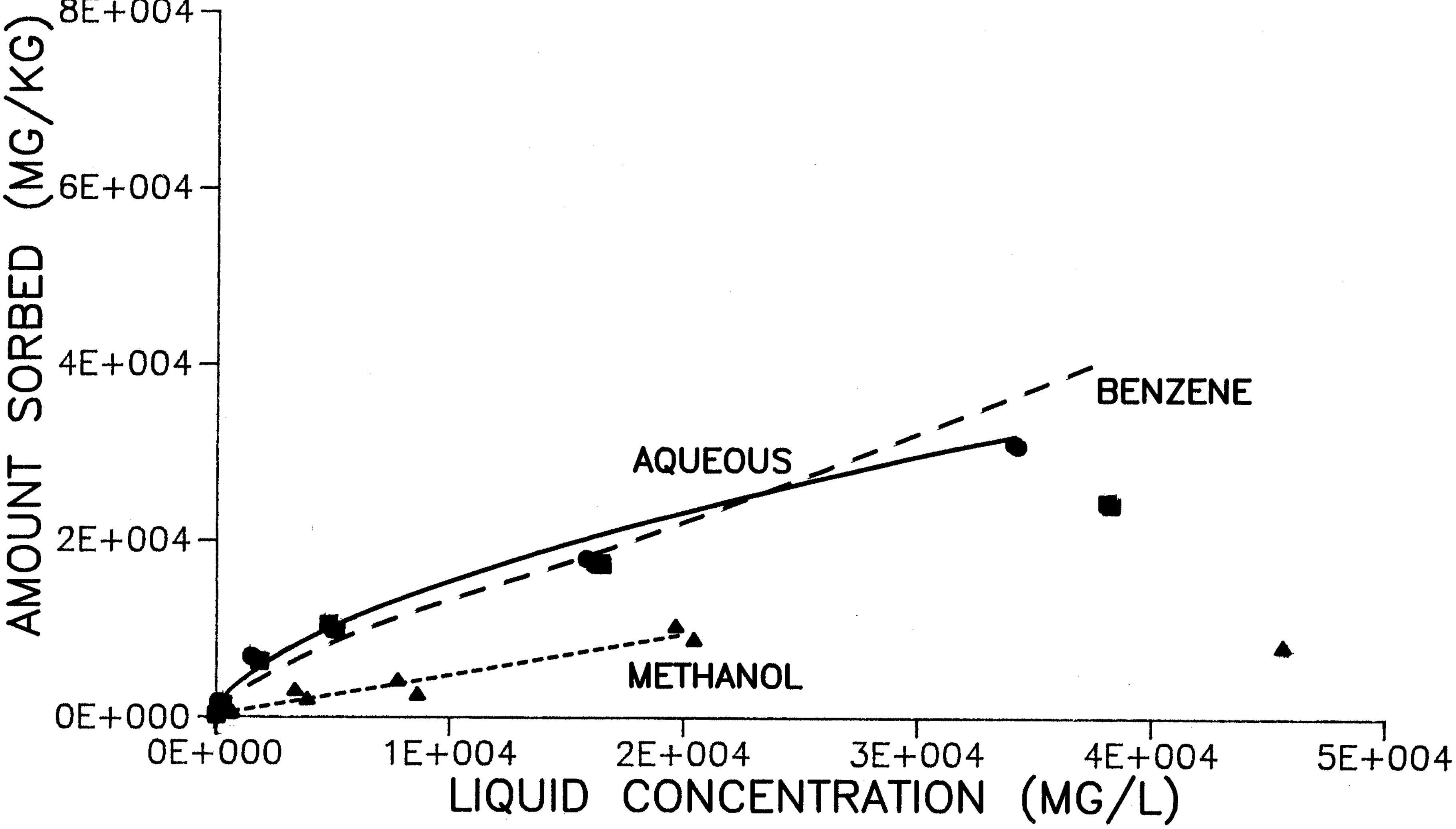


FIGURE 4–7.
PHENOL SORPTION TO NATURAL ZEOLITE

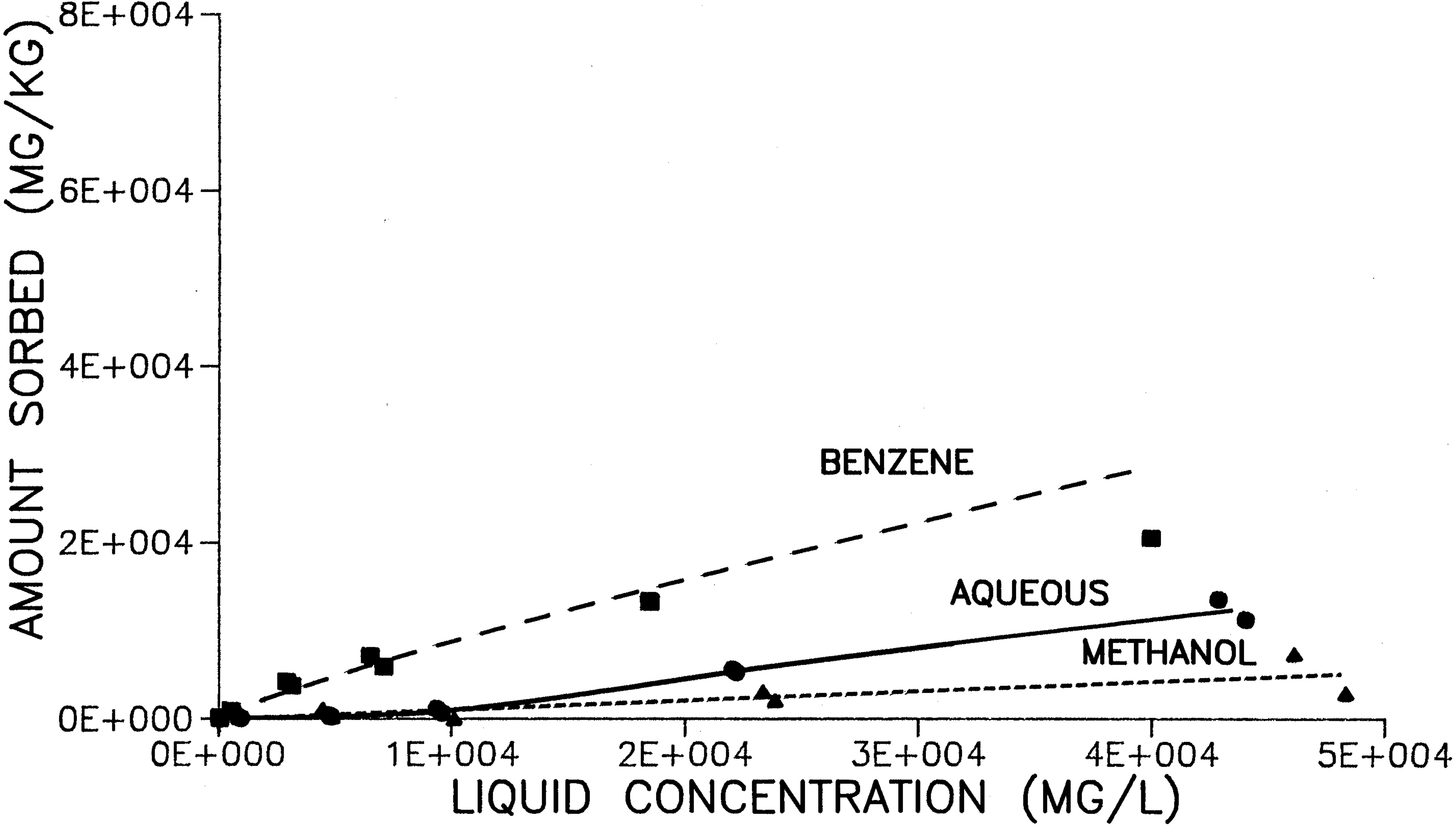
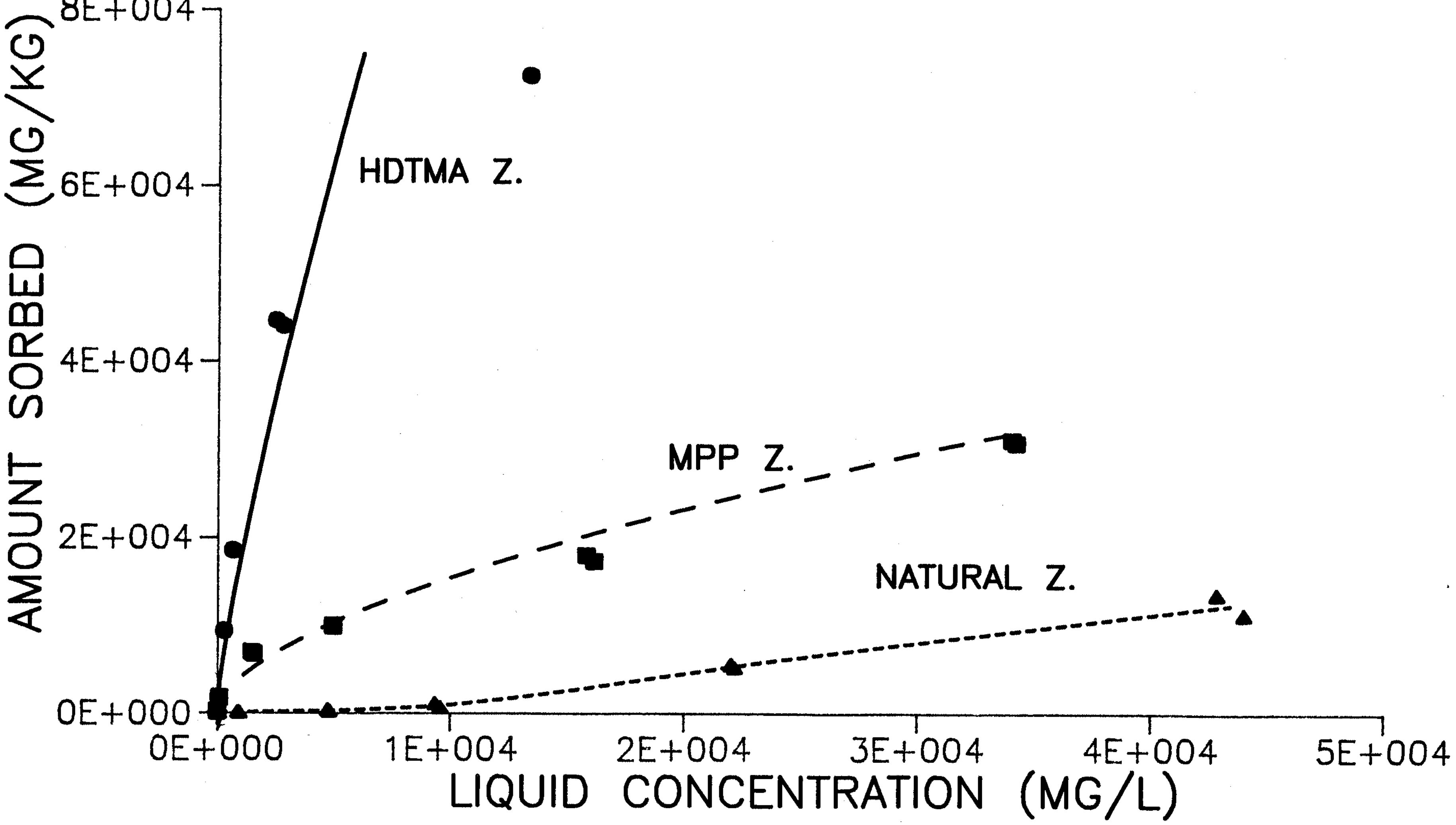


FIGURE 4—8.
PHENOL SORPTION FROM AQUEOUS SOLUTION



HDTMA-zeolite still showed stronger Ph sorption than the MPP-zeolite. The Freundlich equation (Eq. [2-5]) best-fit Ph sorption data to HDTMA- and MPP-zeolite. Curves shown in Fig. 4-5 through 4-8 are these best-fit Freundlich isotherms. Best-fit parameters for all isotherms are summarized in Table 4-2. Cowan and White (1962) found the Freundlich equation also best-fit Ph sorption data to dodecylammonium-montmorillonite. They measured exothermic Ph sorption, and presented data they interpreted as evidence showing that both interactions between the phenyl group and amine organic chains, and between the hydroxyl group and the mineral surface, contribute to sorption. In contrast, Mortland et al. (1986) found no Ph sorption to HDTMA-, TMA-, or hexadecylpyridinium-montmorillonite from aqueous solution. They attributed the lack of Ph sorption to strong solute-solvent hydrogen bonds that prevented Ph from being removed from water. However, the maximum Ph concentration they evaluated was less than 95 mg/L, while in this study, the minimum Ph concentration evaluated was 100 mg/L. It may be that at very low concentrations, hydrogen bonding between Ph and water dominates over other mechanisms, while at much greater Ph concentrations, the hydrophobicity of the phenyl group dominates, when there may not be enough water to fully solvate the Ph.

Table 4-2. Best-fit Isotherm Parameters for Ph Sorption.

Zeolite	Solvent	log K_F	N	K_d
HDTMA	Aqueous	1.80	0.81	--
	Benzene	2.30	0.57	--
	Methanol	--	--	0.45
MPP	Aqueous	1.83	0.59	--
	Benzene	1.45	0.67	--
	Methanol	--	--	0.46
Natural	Aqueous	--	--	--
	Benzene	0.50	0.86	--
	Methanol	--	--	0.11

The sorption isotherm to the natural zeolite is slightly S-shaped (see Fig. 4-8). S-shaped isotherms for Ph sorption from water have been observed by McBride et al. (1977) for sorption to TMA-clay, and by Mortland et al. (1986) for sorption to PTMA-clay. In fact, an S-shaped type isotherm is commonly seen for Ph sorption from water to any polar substrate (Giles et al., 1960). The S-isotherm typically indicates a strong solute-solvent interaction (in this case via hydrogen bonds), with competition for mineral surface sorption sites. Once sorbed, however, interactions between the sorbed species and dissolved solutes promotes cooperative sorption, and sorption increases (Giles et al., 1974). Infrared analyses of sorbed alcohols have shown that the alcohols do not sorb to surfaces via hydrogen bonds between silica hydroxyl groups and alcohol groups. Rather, the alcohols compete with water for ligand positions in solvation shells around exchangable inorganic cations (Mortland, 1970). As a result, the amount of sorption is very dependant on the saturating inorganic cation. In this study, because the zeolites had been subjected to a sodium acetate buffer to remove carbonates, the exchange sites were essentially sodium saturated.

The S-shaped isotherms observed by Mortland et al. (1986) on PTMA zeolite lend support to the concentration-dependant sorption mechanism argument presented above. The Freundlich isotherms observed in this study may in fact truly be S-isotherms, where the lowest part of the curve was not analyzed.

Comparison of Phenol Sorption in Aqueous Solution and in Benzene

As in the aqueous solutions, all isotherms in benzene were Freundlich-type, with most sorption to HDTMA-zeolite, and least to natural zeolite. Freundlich parameters are presented in Table 4-2. Phenol sorption to HDTMA-zeolite from benzene was significantly less than from aqueous solution (Fig. 4-5). Phenol sorption to MPP-zeolite from benzene and aqueous solution was essentially identical except at the highest Ph concentration (Fig. 4-6). Phenol sorption from benzene was actually higher than from aqueous solution to natural zeolite (Fig. 4-7).

Mortland et al. (1986) observed that Ph was actually more strongly sorbed from hexane to a variety of treated clays than from water. They attributed this behavior to the fact that Ph did not interact with hexane as a solvent, and was therefore preferentially sorbed by the organo-clay complex. Once again, the differences in their results and the results from this study may be a concentration-dependant effect, as discussed above. Additionally, because benzene is more similar to Ph than hexane is, there may be some interaction between Ph and benzene, either between aromatic groups, or dipole-π-electron interactions. Alternately, in this study, benzene may compete with Ph for sorption sites on the modified zeolites, thereby reducing Ph sorption in comparison to Ph sorption from aqueous solutions.

Less Ph was sorbed from benzene to the natural zeolite than to the HDTMA- or MPP-zeolites, where a hydrophobic surface medium was present. Nonetheless, Ph is still more strongly removed from benzene than from water to the natural zeolite. This indicates that when no hydrophobic surface is present, the hydrogen bonding in aqueous solution is stronger than the propensity for Ph to be removed. In benzene, however, the interaction between the Ph hydroxyl group and the hydrophilic natural mineral surface is stronger than the solute-solvent interactions between similar functional groups, resulting in increased sorption from the nonpolar solvent.

Phenol Sorption from Methanol

All Ph sorption isotherms from methanol were linear, fit by Eq. [2-1]. As shown in Table 4-2, the K_d's to HDTMA- and MPP-zeolite were nearly identical, while the K_d to natural zeolite was lower. Apparently, both strong hydrogen bonding of alcohol groups and strong nonpolar interactions between the phenyl group and methyl groups of methanol provided a medium strongly favored by Ph, such that removal from methanol was minimal. Again, the presence of a hydrophobic surface medium promoted slightly higher Ph sorption than to a hydrophilic surface.

These data show that the very polar hydroxyl group of Ph plays a significant role in influencing solvent-solute and solute-surface interactions, and therefore considerably impacts the solute sorption at different concentrations and to different surfaces. The presence of a hydrophobic surface enhances Ph sorption, with apparently the more hydrophobic the surface, the more Ph sorption. The similar phenyl groups of the MPP ion apparently do not influence Ph sorption more than the overall hydrophobicity of the surface-altering agent.

Ethylbenzene, PCE, and TCA Sorption Assessment

General Isotherm Comparisons

Figures 4-9 through 4-17 show several trends. In organic solvents, Eben, TCA, and PCE were not sorbed to any of the zeolites. Sorption from benzene in particular was zero in all cases. Benzene effectively solvated all these molecules to the extent that sorption into the surface hydrophobic medium was not preferred. While slight sorption of TCA to natural and MPP-zeolite, and of Eben to natural zeolite, was seen from methanol, the extent of this sorption was very small relative to sorption from aqueous solution. The small amount of observed sorption may be because TCA and Eben can compete with methanol for polar surface sorption sites. Nonpolar PCE was not sorbed, because it cannot compete with methanol for mineral surface sites.

Also evident from the figures is that duplicate agreement was not exact, and some values of sorption from organic solvents actually indicated a negative sorption. Although blank samples were run at every concentration and used as the initial sample concentration, it is likely that a major contributor to different duplicate values was differential volitilization from separate samples during equilibration. In the aqueous samples, it appeared as though the organic solute volatilized, because blank samples were generally slightly less than their calculated concentration. (Initial solute concentrations were calculated based on the stock solution volume and the amount of organic solute added to it). In the organic solvents, however, the reverse appeared to be the case. That is, the organic solvent appeared to volatilize, resulting in a solute concentration slightly higher than the calculated initial concentration. Apparently, in some organic solvent samples, solvent in zeolite samples volatilized slightly more than the blanks, giving the appearence of negative sorption. In general, blank concentration values were within about 85% of the calculated values in aqeuous solution, and ranged from about 95-120% of the calculated value in organic solvents. The exception was Eben, where a few aqueous samples had a blank recovery of less than 70%. While the septum method minimizes volatilization loss, the effect of initially piercing the septum to inject the solution does allow for some volatilization. This volatilization can be easily identified and corrected for using blank samples, however. Other potential contributors to inexact duplicate

greater volatilization for Eben could be reflected as greater apparent sorption

FIGURE 4—9.
PCE SORPTION TO HDTMA ZEOLITE

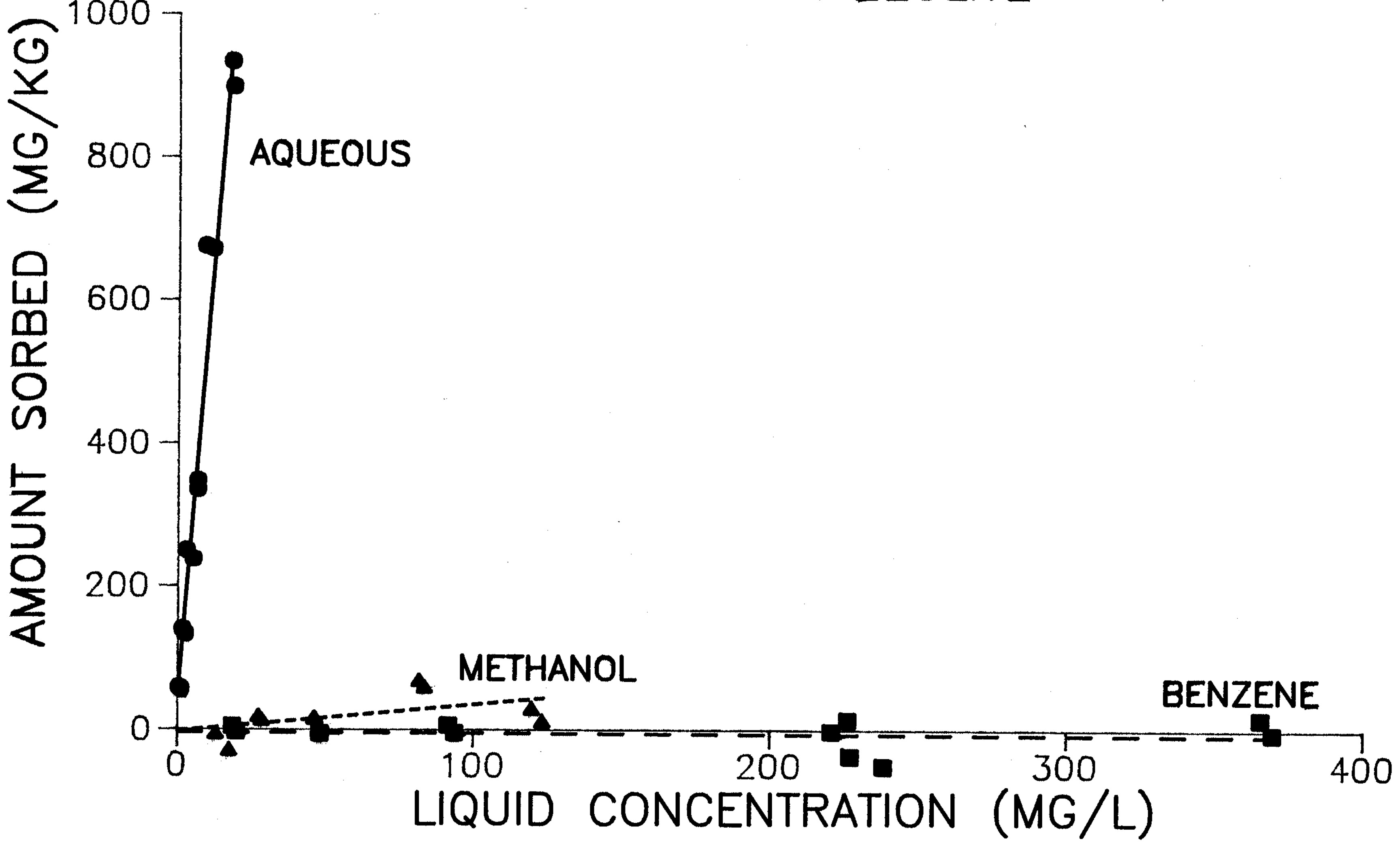


FIGURE 4—10.
PCE SORPTION TO MPP ZEOLITE

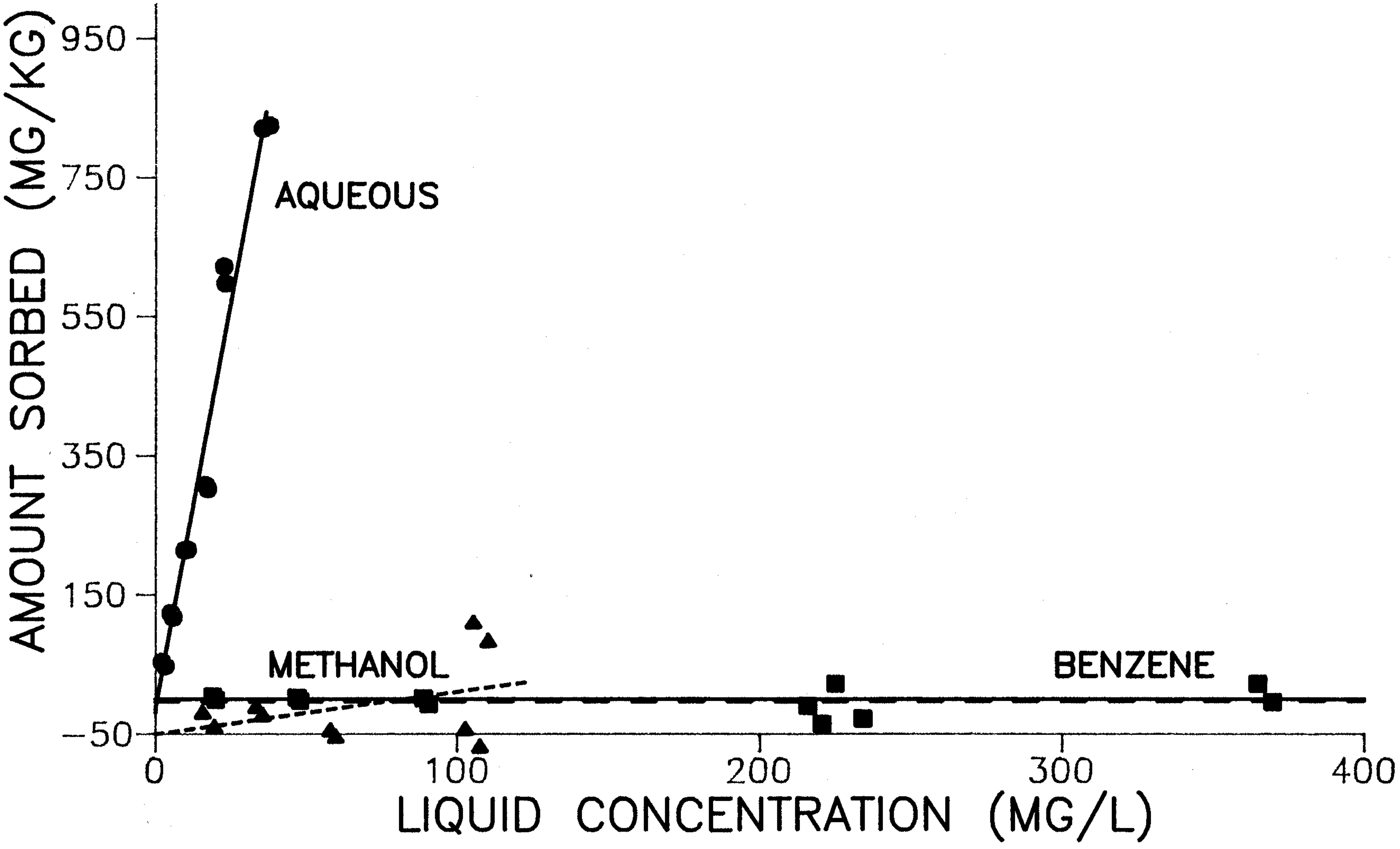


FIGURE 4–11.
PCE SORPTION TO NATURAL ZEOLITE

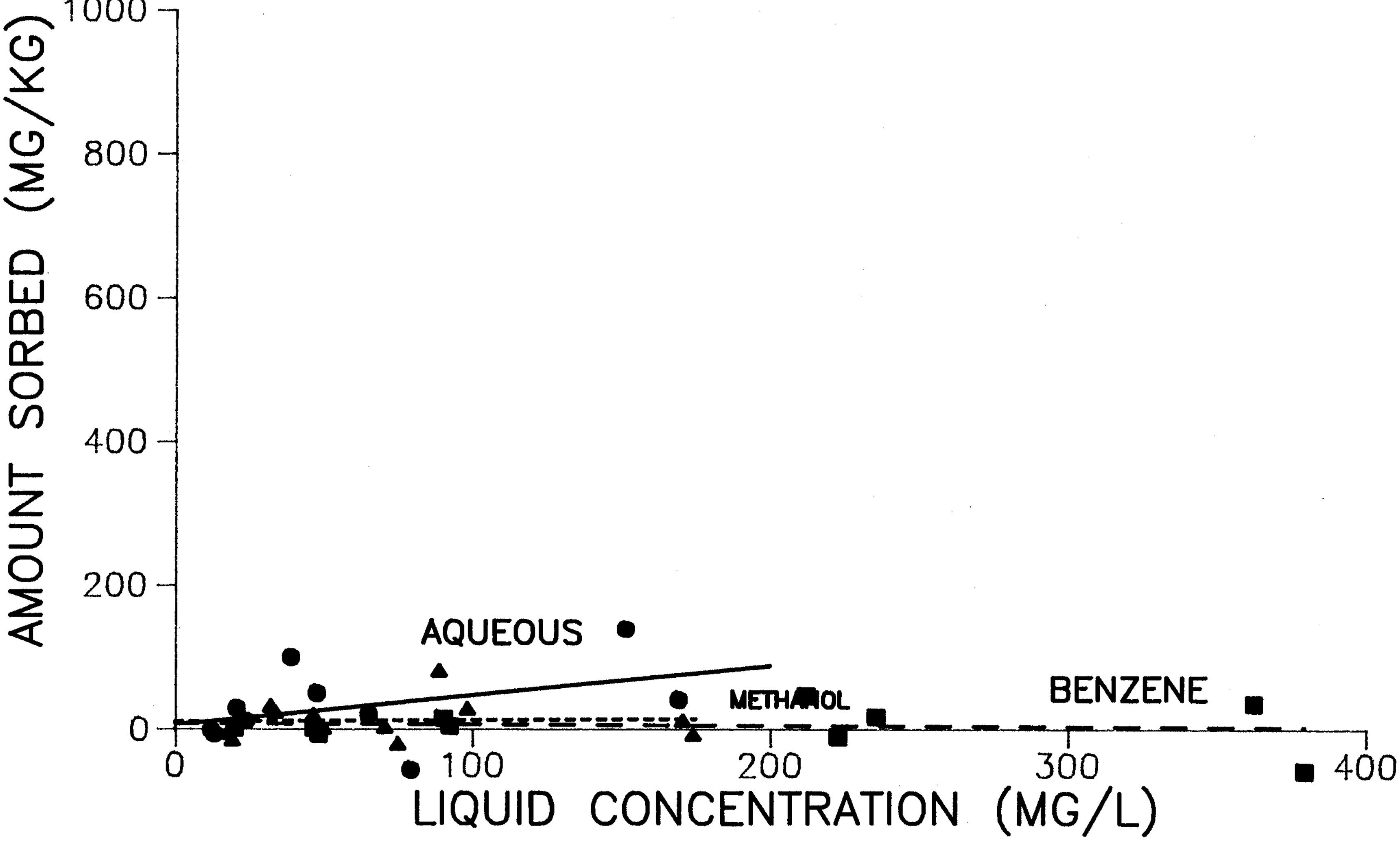


FIGURE 4—12.
EBEN SORPTION TO HDTMA ZEOLITE

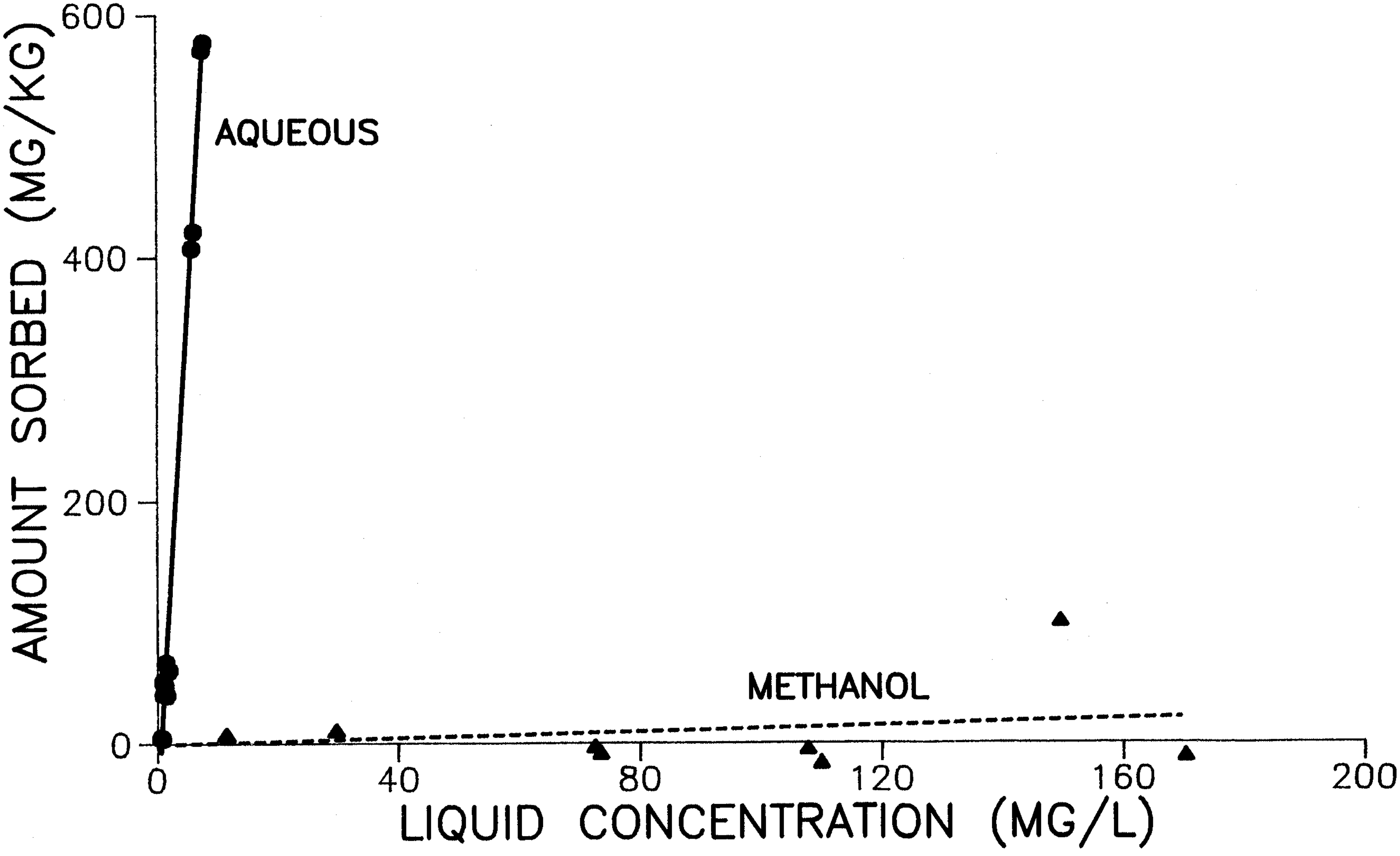


FIGURE 4–13.
EBEN SORPTION TO MPP ZEOLITE

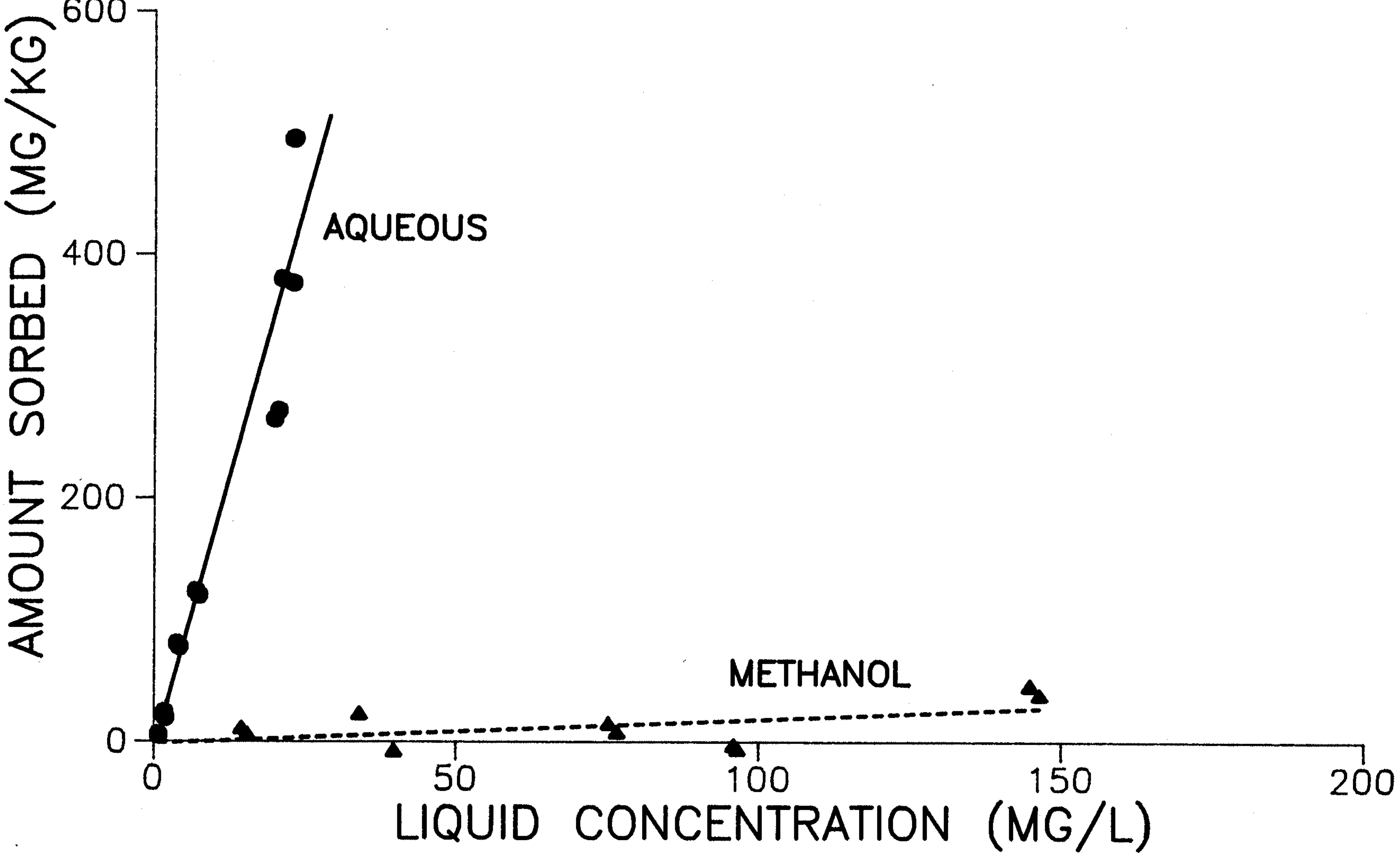


FIGURE 4–14.
EBEN SORPTION TO NATURAL ZEOLITE

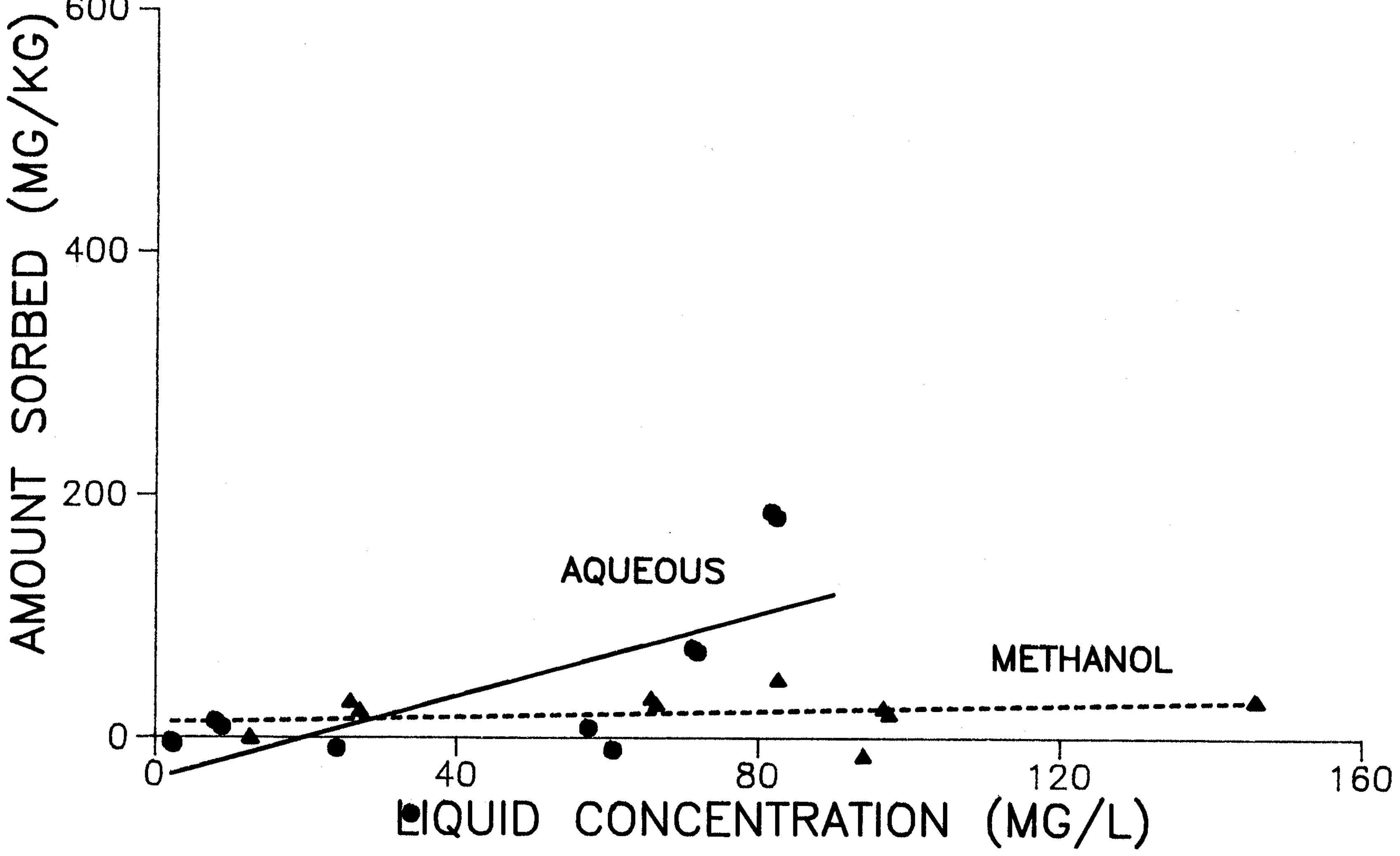


FIGURE 4—15.
TCA SORPTION TO HDTMA ZEOLITE

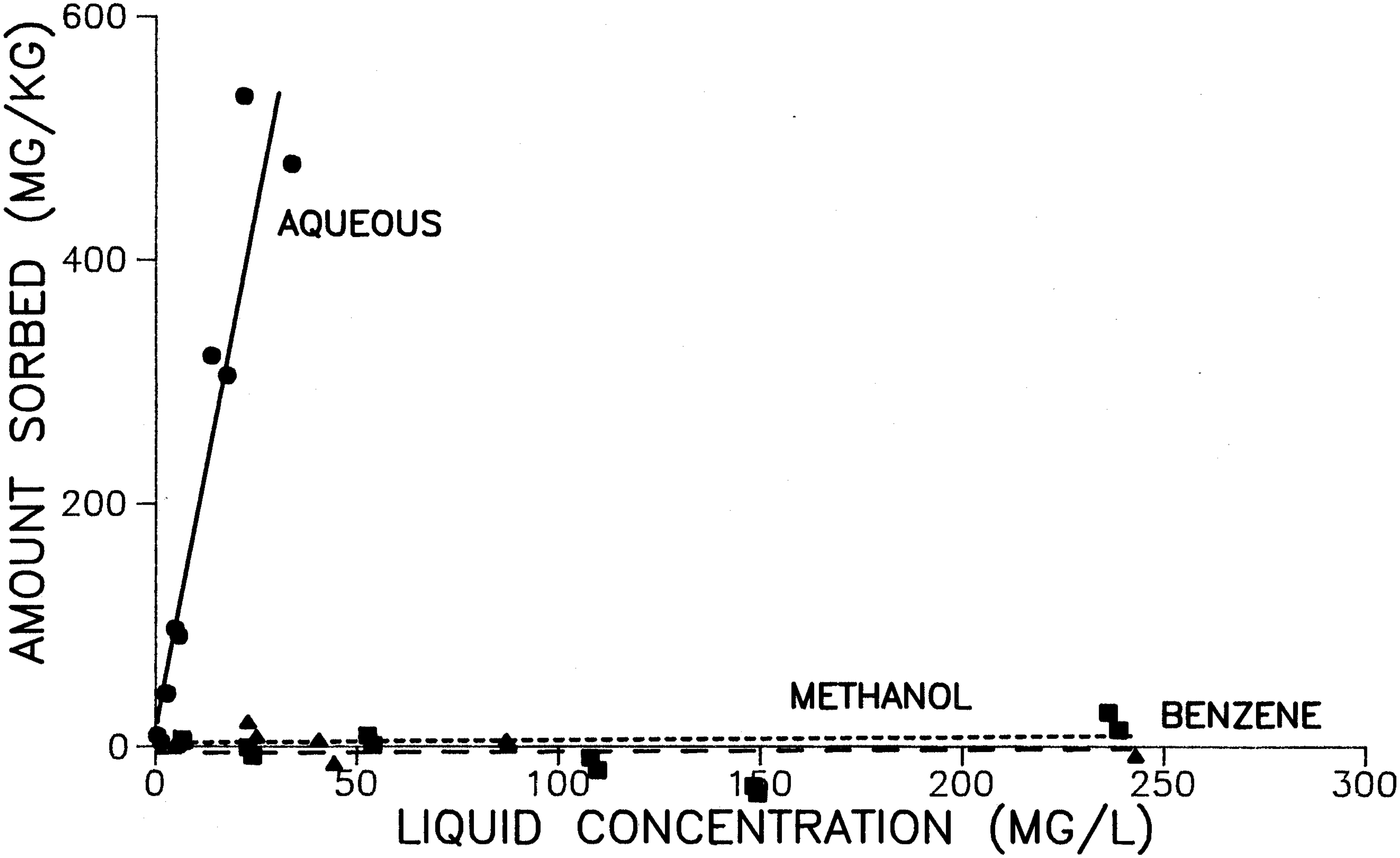


FIGURE 4–16.
TCA SORPTION TO MPP ZEOLITE

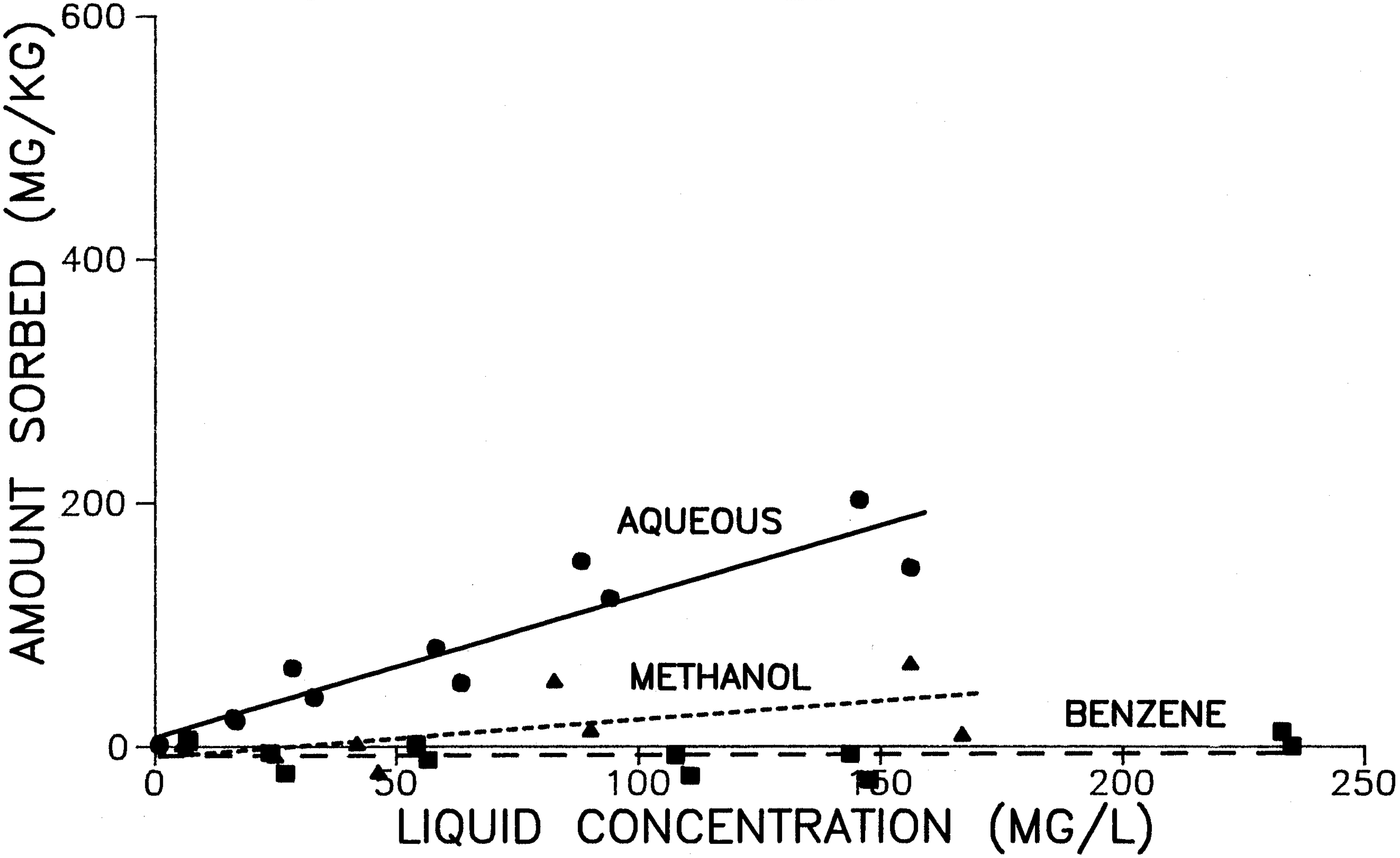
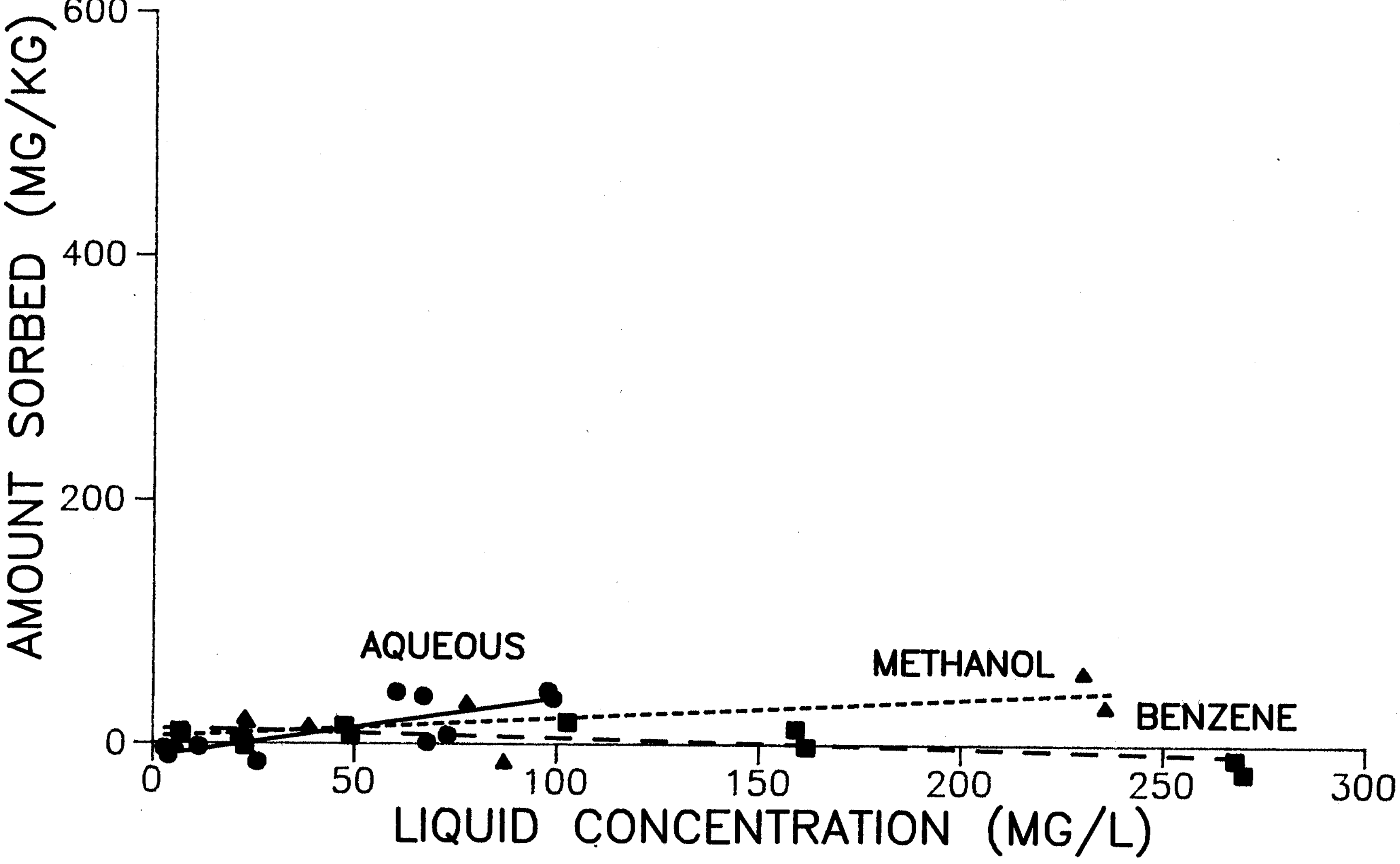


FIGURE 4—17.
TCA SORPTION TO NATURAL ZEOLITE



agreement include sample heterogeneity, volatilization losses during solution transfers, and slight differences in GC sensitivity between samples. Because the overall sorption from organic solvents was negligible, the remaining discussion will focus on sorption from aqueous solution.

Comparison of Quantitative Isotherm Parameters

To facilitate rapid visual comparisons of sorption to the different zeolite treatments from aqueous solution, a comparison of the different zeolites is presented as Fig. 4-18 through 4-20. Quantitative isotherm parameters from fits of Eq. [2-1] and [2-6] are presented in Table 4-3. Log K_{oc}'s were calculated using the measured values of organic carbon of 6.3% for HDTMA, 3.8% for MPP, and 0.16% for natural zeolite. Log K_{om}'s were calculated using a correction factor of 1.25 for HDTMA, 1.18 for MPP, and 2.0 for natural zeolite (the correction factors were determined simply from the ratio of total cation mass to organic carbon mass. The correction factor of 2.0 for natural organic carbon was estimated per Nelson and Sommers, 1982). Literature values of log K_{oc} and log K_{ow} from Table 3-1 are presented for comparison.

Table 4-3. Summary of Linear Isotherm Parameters.

		Organic Solute		
Parameter	Treatment	PCE	Eben	TCA
K_d	HDTMA	50.04	80.18	17.11
	MPP	23.36	18.01	1.16
	Natural	0.41	1.69	0.49
log K_{oc}	HDTMA	2.90	3.10	2.43
	MPP	2.79	2.68	1.48
	Natural	2.41	3.02	2.49
log K_{om}	HDTMA	2.80	3.00	2.33
	MPP	2.72	2.61	1.41
	Natural	2.11	2.72	2.19
Literature log K_{ow}	--	2.60	3.15	2.47
Literature log K_{oc}	--	2.56	2.28	2.30

FIGURE 4–18.
PCE SORPTION FROM AQUEOUS SOLUTION

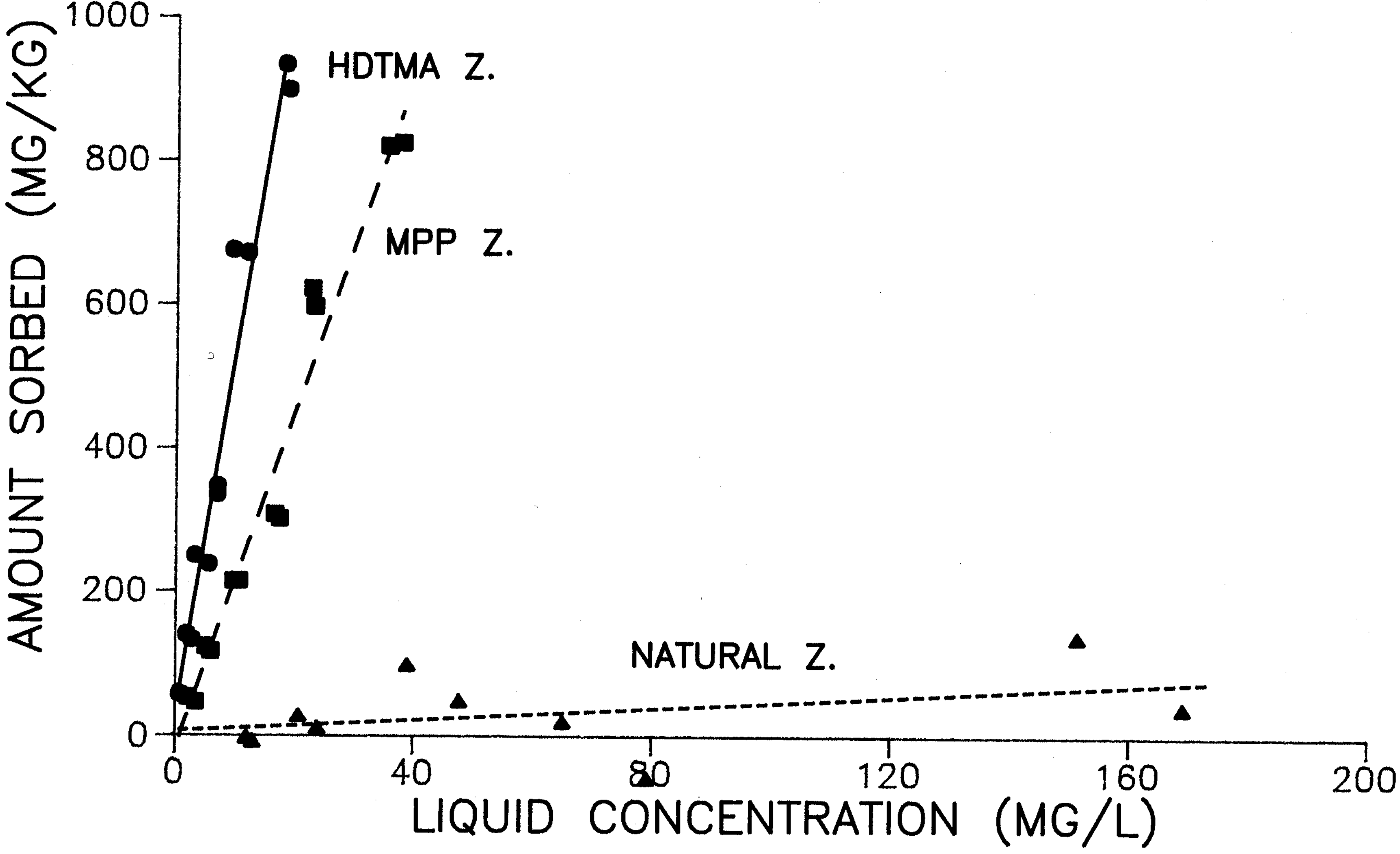


FIGURE 4–19.
TCA SORPTION FROM AQUEOUS SOLUTION

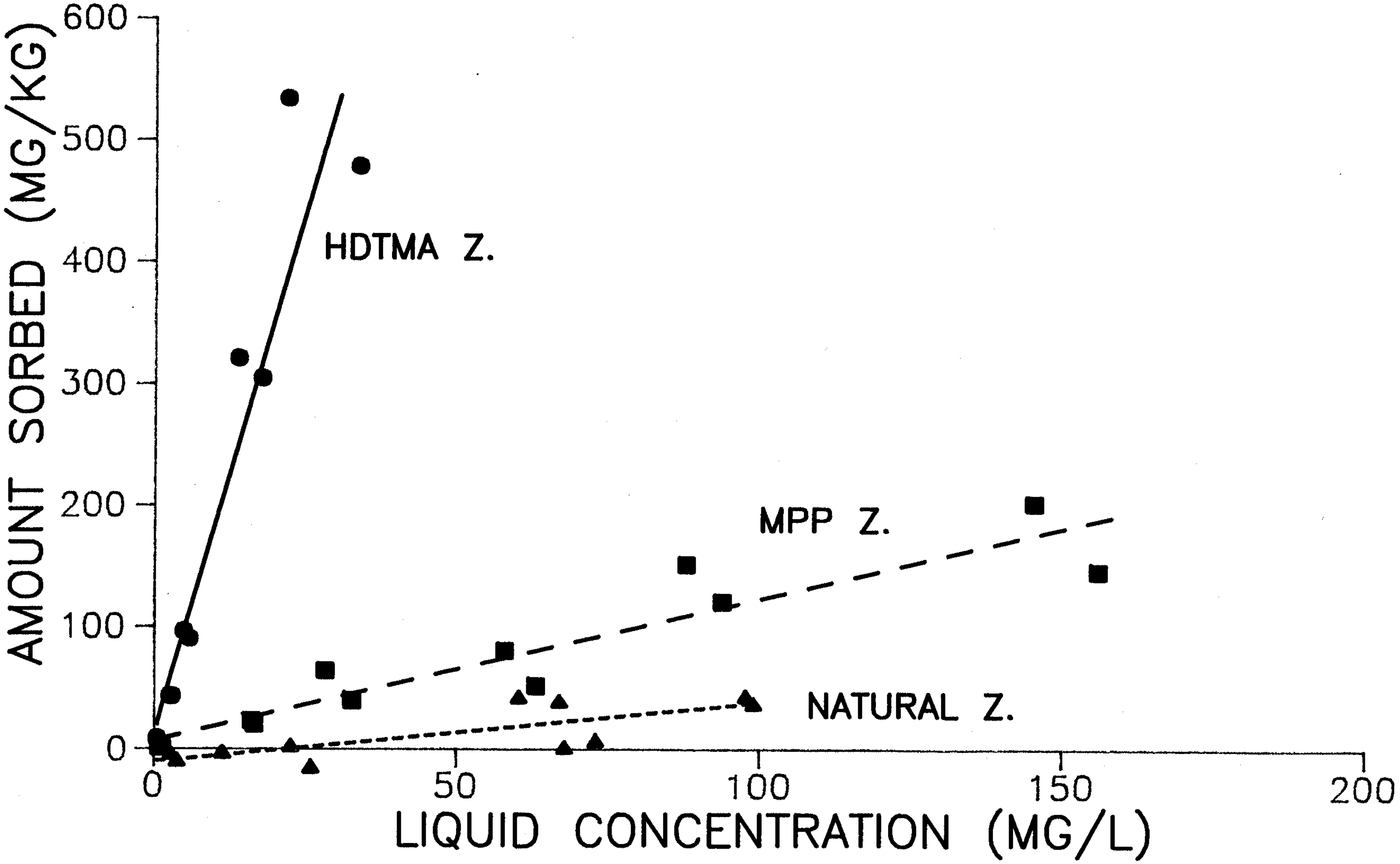
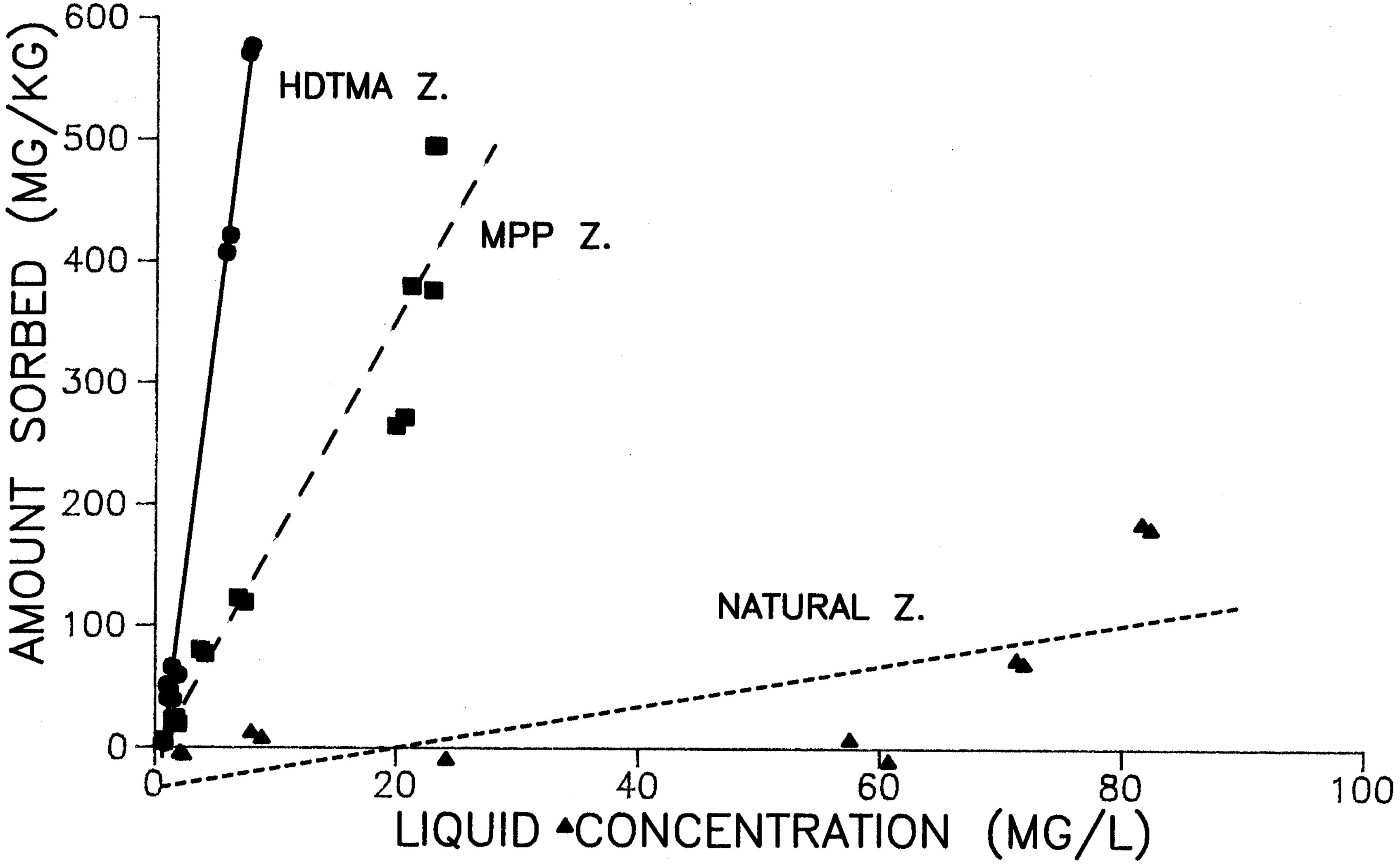


FIGURE 4—20.
EBEN SORPTION FROM AQUEOUS SOLUTION



Evident from these figures and from the data presented in Table 4-3 is that treated zeolites are much more effective sorbents for all solutes than identical untreated materials. The much larger K_d values on the treated zeolites over the natural zeolite support this assertion. The increase in K_d with an increase in organic carbon content of the surface-altering agent suggests the sorption of all three solutes was controlled primarily by the zeolite organic carbon content. Indeed, when the K_d's are normalized by the fraction of organic carbon, the resulting log K_{oc}'s agree fairly well. The variability in K_d is reduced from over 2 orders of magnitude to less than one half an order of magnitude variability in K_{oc}. (The one exception is TCA sorption to MPP-zeolite, which will be discussed separately).

A comparison of literature log K_{oc}'s to these measured log K_{oc}'s similarly shows overall good agreement, generally within one half order of magnitude (again, TCA sorption to MPP-zeolite is an exception). The observed log K_{oc}'s to the treated zeolites, however, are generally higher than the reported values, especially for sorption to HDTMA-zeolite. This may indicate that such surface-altering agents are a more effective partitioning medium than natural organic matter, as suggested by Boyd et al. (1988a, 1988b, 1988c) and Toro-Suarez et al. (1990). These researchers cited a good correlation between log K_{om}'s and log K_{ow}'s as evidence supporting a partitioning-type sorption mechanism. Comparison of the log K_{ow}'s for Eben, TCA, and PCE to the observed log K_{om}'s for these compounds (Table 4-3), similarly shows reasonable agreement, again within about a half-order of magnitude. HDTMA-zeolite showed particularly good agreement between log K_{om}'s and log K_{ow}'s (within a factor of 1.6). Agreement between log K_{ow}'s to MPP-zeolite log K_{om}'s was not quite as good, suggesting either that MPP does not create as efficient a partitioning medium as HDTMA does, or that the aromatic MPP is not as an attractive medium for the sorption of these aliphatic solutes.

The fact that MPP-zeolite was a less effective sorbent than HDTMA-zeolite, and the corresponding low sorption of TCA to MPP-zeolite may be due to several factors. The measured MPP-zeolite organic carbon content was only about 92% of the theoretical organic carbon content at complete MPP saturation. This could indicate incomplete exchange and exposed mineral surface. When the surface is not completely covered to form a continuous hydrophobic medium, sorption of dissolved organic compounds is often less efficient (Mortland et al., 1986). Sorption of TCA may be reduced because TCA may undergo dipole-dipole interactions with water, and MPP is not enough of a hydrophobic medium to induce TCA sorption. In this respect, Eben and PCE could be sorbed, because they do not have dipole moments as high as TCA, and would not interact with water. In addition, the solubilities of Eben and PCE are an order of magnitude less than TCA solubility (see Table 3-1), so they would not likely require a surface medium as hydrophobic to induce sorption. Finally, TCA may have been sterically hindered from access to some sorption sites by the large, relatively rigid phenyl groups of MPP.

In contrast, HDTMA apparently fully covered the mineral external surfaces, creating a continuous hydrophobic medium. This was evidenced by the following: HDTMA-zeolite was the strongest sorbent for all solutes, log K_{oc}'s for all compounds to HDTMA-zeolite were nearly a half-order of magnitude higher than log K_{oc}'s reported for these compounds to natural organic matter, and results of the organic carbon measurement indicated essentially 100% exchange of HDTMA to surface sorption sites. These facts, along with the observation that neither Eben nor Ph were preferentially sorbed to MPP-zeolite, suggest that the overall surface coverage and resulting hydrophobicity was more important than the nature of the surface-altering agent functional group in influencing sorption.

The very small sorption to natural zeolite (based on K_d's), and the good agreement of measured K_{oc}'s to literature values (within a factor of 5.5), even at low organic carbon content, suggests that the sorption contributed by the zeolitic internal channels was negligible in comparison to that contributed by the organic carbon. Sorption to the treated zeolites also supported this conclusion. Estimates of molecular sizes were made to evaluate whether the organic compounds were excluded from zeolitic channels, or not sorbed. Results of the estimated molecular dimensions, presented in Table 4-4, show that all the organic solutes, with the possible exception of Eben (which has molecular dimensions very close to the largest channel openings), should not be excluded from zeolitic channels due to size restrictions. Molecular size calculations were made assuming phenyl groups are perfectly planar hexagons, PCE is perfectly planar, and all tetrahedrally coordinated carbons form perfect tetrahedra. While these assumptions are oversimplifications, they can provide a rough estimate of molecular dimensions. Bond angles and covalent bond radii were obtained from Pauling (1967). Although the sorption isotherms suggest negligible zeolitic molecular selectivity for these compounds, additional spectroscopic data such as infrared spectra of sorbed species (see Mortland, 1970 and 1986), or XRD data on clay layer spacings, could be collected to better identify sorption mechanisms and sites on untreated mineral surfaces, respectively.

Table 4-4. Molecular Size Estimates.

Molecule	Dimensions (Å)
Phenol	5.55 x 4.28 x 0.93
PCE	3.32 x 2.92
TCA	2.49 x 2.68 x 2.88
Eben	3.71 x 6.11 x 7.43
Maximum Clinoptilolite channel opening (Å):	4.4 x 7.2

Estimates of K_{oc} from Solute Properties

Many researchers have noticed an empirical correlation between solute properties and K_{oc} among structurally similar compounds. Specifically, correlations between aqueous solubility (S_{aq}) and K_{ow}, or between K_{ow} and K_{oc} typically give estimates within an order of magnitude of measured K_{oc}'s. Because the overall relationship between observed and literature K_{oc}'s for the compounds evaluated in this study was within this range, it may be possible to estimate the K_{oc}'s for these compounds from other properties. Karickhoff et al. (1979), Karickhoff (1981), Hasset et al. (1980), Briggs (1981), and Chiou et al. (1983), derived empirical and semi-empirical relationships for a range of aromatic compounds. Chiou et al. (1979) derived a relationship between K_{oc} and S_{aq} among a number of halogenated compounds, including chlorinated benzenes, TCE, TCA, tetrachloroethane, and brominated propanes. Equations derived by these researchers were evaluated and compared to the measured results from this study.

Because only three compounds were evaluated in this study, and they are not structurally similar, (they were chosen because they were structurally different), no attempt was made to derive a K_{oc}-K_{ow} or K_{oc}-S_{aq} relationship from the database generated in this study. In fact, correlations between groups of structurally different compounds may not be valid, as different sorption mechanisms may dominate for groups of different structural classes (Mingelgrin and Gerstl, 1983).

In general, correlations between K_{oc} and K_{ow} give better results than correlations of K_{oc} with S_{aq}, the latter which often give results only within no better than an order of magnitude (Karickhoff, 1981). Often, correlations based on aqueous solubility give better overall results when a "crystal energy" term is added (Karickhoff, 1981). However, a crystal energy term is usually only necessary for large, high melting-point solids, and this term is usually assumed to be zero for organics that are liquid at 25 °C (Gschwend and Wu, 1985; Karickhoff, 1981).

Surprisingly, the best overall agreement between estimated and observed K_{oc}'s for compounds analyzed in this study was given by the correlation between log K_{oc} and log S_{aq} developed by Karickhoff et al. (1979) for 10 different aromatic compounds. The correlation between log K_{oc} and log K_{ow} presented in the same paper was also reasonable. The correlations from Chiou et al. (1979), which would be expected to be best for the chlorinated compounds TCA and PCE gave reasonable results, but did not predict the measured values as accurately as the Karickhoff et al. equations. These two sets of equations and their predicted log K_{oc} values are presented in Table 4-5.

Comparisons of predicted data from these equations in Table 4-5 and observed data in Table 4-3 shows that although agreement is not perfect, it is always within an order of magnitude, and often agreement is within about half an order of magnitude. As expected, predictions from the Chiou et al. (1979) equation are better for PCE and TCA than for Eben. However, these predictions are still not as accurate as those from the Karickhoff equations, especially with respect to sorption to HDTMA-zeolite. In general, however, these estimates show that predictive equations may provide a reasonable first estimate for sorption parameters when no other data are available.

Table 4-5. Predicted K_{oc}'s from Organic Solute Properties.

Equation	Predicted log K_{oc} PCE	Eben	TCA
Karickhoff et al., 1979			
$\log K_{oc} = -0.54 \log S_{aq} + 0.44$ (S_{aq} in Mole fraction)	3.03	2.93	2.46
$\log K_{oc} = \log K_{ow} - 0.21$	2.39	2.94	2.26
Chiou et al., 1979			
$\log K_{oc} = -0.56 \log S_{aq} + 4.04$ (S_{aq} in μmoles/L)	2.38	2.28	1.80

V.

SUMMARY AND CONCLUSIONS

SUMMARY

Zeolites were treated with different large organic cations to create a hydrophobic surface medium that would enhance the sorption of dissolved organic compounds. Two different organic cations, HDTMA and MPP, were used to alter the surface hydrophobicity. The HDTMA ion emphasized the alkyl group, while the MPP ion emphasized the aromatic structure. The organic cations were sorbed up to the external CEC, but did not enter into the zeolitic channels. Treating the surfaces significantly increased the zeolite organic carbon content from 0.16% to 6.3% with HDTMA and 3.8% with MPP.

Once sorbed, the organic cations were not significantly desorbed in a variety of pH buffers, inorganic salt solutions, and organic solvents. In general, HDTMA was more strongly bound to the surface than MPP. A large excess of other organic cations was effective in desorbing as much as 30% of the originally bound cations.

Sorption of phenol followed Freundlich-type isotherms, with most the phenol sorbed to the HDTMA-zeolite, and least sorbed to the natural zeolite. Phenol sorption was strongest from aqueous solutions at the concentrations evaluated. Isotherms for the other organic solutes were highly linear, again with stongest sorption to HDTMA-zeolite. K_{om} values for sorption of all species to HDTMA-zeolite were higher than the K_{om} values for the other two zeolites, and were about a factor of 2-5 higher than reported literature K_{om} values. K_{om} values for MPP and natural zeolite were within a factor of approximately 2 of those reported in the literature. The measured log K_{om} values for all compounds to HDTMA-zeolite agreed well with literature values for log K_{ow} for these compounds. Empirical equations developed by others gave reasonable estimates of log K_{oc} values for these compounds to the treated zeolites.

CONCLUSIONS

Interpretation of the results led to several conclusions. In summary, these were:

- Large organic cations will quantitatively exchange for inorganic cations on available mineral surface sites.

- The exchange of such large organic cations onto the mineral surface results in a significant increase in organic carbon content.
- Once sorbed, these organic cations are essentially irreversibly bound.
- Such hydrophobically treated materials are much more effective sorbents for neutral organic compounds than identical untreated materials.
- The extent of organic compound sorption to these modified surfaces is controlled primarily by the amount of surface organic carbon.
- The sorption mechanism is dominated by a partitioning into the surface hydrophobic medium, especially with HDTMA as the surface-altering agent.
- The nature of the surface-altering agent functional groups is not as important as the overall hydrophobicity imparted to the mineral in influencing the extent of nonionic organic compound sorption.
- HDTMA appears to create a continuous hydrophobic medium on the mineral surface that more effectively sorbs organic compounds than MPP treated surfaces or natural soil organic matter.
- Organic solute properties are important in determining the nature and extent of sorption. Specifically, the phenol hydroxyl group can hydrogen-bond with water, resulting in different sorption behavior than low-solubility, nonpolar organic compounds. In general, compound polarity affects the nature and extent of sorption.
- Zeolites do not display molecular selectivity for any of the compounds evaluated.
- When no other data are available, reasonable estimates of log K_{oc}'s may be obtained from empirically derived correlations between log K_{oc} and aqueous solubility or log K_{ow}.

SUGGESTIONS FOR FUTURE WORK

The results of this project indicate that surface-altered minerals are effective sorbents for organic compounds. As a result, they have potential application as ammendments to clay landfill liners or slurry containment walls to immobilize organic contaminant releases. Alternately, they may be employed as selective sorbents for water treatment. Continued research on these areas of application are merited. Because zeolites are known to be excellent sorbents for inorganic heavy metals, the use of modified zeolites such as those used in this project could be, (and are being), investigated for their use as sorbents of mixed wastes that contain both organic and inorganic species.

In addition, because the large particle size of these zeolites makes them amenable for dynamic flow studies such as column studies, this research could be extended with column experiments. As always, the database of sorption data to such modified surfaces could also be extended by evaluating the sorption properties of other organic compounds to these materials. Additional spectroscopic data identifying the locations of sorbed species, (eg., XRD analyses), and types of surface bonds, (eg., IR analyses), could also be collected. Although the short-term stability of these treated surfaces was thoroughly documented in this study, long-term studies of resistance to biodegradation remain to be done. In summary, many aspects of this type of research remain to be studied, and this field promises many new discoveries in the coming years.

VI.

REFERENCES

Aldrich Chemical Co. (1990) *Catalog Handbook of Fine Chemicals:* Aldrich Chemical Co., Inc., Milwaukee, WI, 2150 pp.

Alther, G.R., Evans, J.C., and Pancoski, S.E. (1990) No feet of clay: *Civil Eng.* **August,** 60-61.

American Public Health Assoc. (1960) *Standard Methods for the Examination of Water and Wastewater, 11th ed.,* American Public Health Assoc., Inc., New York, 79-81.

Ames, L.L. Jr. (1960) Cation sieve properties of clinoptilolite: *Am. Mineralogist* **45,** 689-700.

Banerjee, S., Yalkowsky, S.H., and Valvani, S.C. (1980) Water solubility and octanol/water partition coefficients of organics. Limitations of the solubility-partition coefficient correlation: *Environ. Sci. Tech.* **14,** 1227-1229.

Barrer, R.M. (1978) *Zeolites and Clay Minerals as Sorbents and Molecular Sieves:* Academic Press, London, 497 pp.

Barrer, R.M. and Brummer, K. (1963) Relations between partial ion exchange and interlamellar sorption in alkylammonium montmorillonites: *Trans. Faraday Soc.* **59,** 959-968.

Barrer, R.M. and Hampton, M.G. (1957) Gas chromatography and mixture isotherms in alkylammonium bentonites: *Trans. Faraday Soc.* **53,** 1462-1475.

Barrer, R.M. and MacLeod, D.M. (1955) Activation of montmorillonite by ion exchange and sorption complexes of tetra-alkylammonium montmorillonites: *Trans. Faraday Soc.* **51,** 1290-1300.

Barrer, R.M. and Millington, A.D. (1967) Sorption and intracrystalline porosity in organo-clays: *J. Colloid Interface Sci.* **25,** 359-372.

Barrer, R.M., Papadopoulos, R., and Rees, L.V.C. (1967) Exchange of sodium in clinoptilolite by organic cations: *J. Inorg. Nucl. Chem.* **29,** 2047-2063.

Barrer, R.M. and Perry, G.S. (1961a) Sorption of mixtures, and selectivity in alkylammonium montmorillonites. I. Monomethylammonium bentonite: *J. Chem. Soc.* 842-849.

Barrer, R.M. and Perry, G.S. (1961b) Sorption of mixtures, and selectivity in alkylammonium montmorillonites. II. Tetramethylammonium montmorillonite: *J. Chem. Soc.* 850-858.

Barrer, R.M. and Reay, J.S.S. (1957) Sorption and intercalation by methylammonium montmorillonites: *Trans. Faraday Soc.* **53,** 1253-1261.

Black, W. (1969) Basic chemistry of surface-active agents: in *Water Repellent Soils,* L.F. DeBano and J. Letey, eds., Proc. Symp. Water-Repellent Soils, U. Calif. Riverside, May 6-10, 1968, pp. 133-142.

Bohn, H.L, McNeal, B.L, and O'Connor, G.A. (1985) *Soil Chemistry, 2nd ed.:* John Wiley and Sons, New York, 341 pp.

Bouchard, D.C., Powell, R.M., and Clark, D.A. (1988) Organic cation effects on the sorption of metals and neutral organic compounds on aquifer material: *J. Env. Sci. Health (A)* **23,** 585-601.

Boyd, S.A., Lee, J., and Mortland, M.M. (1988a) Attenuating organic contaminant mobility by soil modification: *Nature* **333,** 345-347.

Boyd, S.A., Mortland, M.M., and Chiou, C.T. (1988b) Sorption characteristics for organic compounds in hexadecyltrimethyl ammonium-smectite: *Soil Sci. Soc. Am. J.* **52,** 652-657.

Boyd, S.A., Shaobai, S., Lee, J., and Mortland, M.M. (1988c) Pentachlorophenol sorption by organo-clays: *Clays and Clay Minerals* **36,** 125-130.

Brandt, G.H. (1969) Soil physical properties altered by adsorbed hydrophobic materials: in *Water Repellent Soils,* L.F. DeBano and J. Letey, eds., Proc. Symp. Water-Repellent Soils, U. Calif. Riverside, May 6-10, 1968, pp. 205-220.

Briggs, G.G. (1981) Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor: *J. Agric. Food Chem.* **29,** 1050-1059.

Cadena, F. (1988) Treatment of water supplies contaminated with toxic pollutants using tailored soils: *New Mexico Water Resources Research Institute,* **Report No. 235** New Mexico State University, Las Cruces, New Mexico, 54 pp.

Cadena, F. (1989) Use of tailored bentonite for selective removal of organic pollutants: *J. Environ. Eng., ASCE* **115,** 756-767.

Cadena, F. and Jeffers, S.W. (1987) Use of tailored clays for selective adsorption of hazardous pollutants: *Proc. 42nd Indus. Waste Conf.* **42,** 113-119, Purdue University, West Lafayette, Indiana.

Chen, N.Y. (1976) Hydrophobic properties of zeolites: *J. Phys. Chem.* **80,** 60-64.

Chiou, C.T., Freed, V.H., Schmedding, D.W., and Kohnert, R.L. (1977) Partition coefficients and bioaccumulation of selected organic chemicals: *Environ. Sci. Technol.* **11,** 475-478.

Chiou, C.T., Peters, L.J., and Freed, V.H. (1979) A physical concept of soil-water equilibria for nonionic organic compounds: *Science* **206,** 831-832.

Chiou, C.T., Porter, P.E., and Schmedding, D.W. (1983) Partition equilibria of nonionic organic compounds between soil organic matter and water: *Environ. Sci. Technol.* **17,** 227-231.

Cowan, C.T. (1963) Adsorption by organo-clay complexes--Part 2: *Clays and Clay Minerals* **10,** 226-234.

Cowan, C.T. and White, D. (1962) Adsorption by organo-clay complexes: *Clays and Clay Minerals* **9,** 459-467.

DeBano, L.F. (1981) *Water repellent soils: A state of the art:* Gen. Tech. Rept. PSW-46, USDA Forest Service Pacific Southwest Forest and Range Experiment Station, 21 pp.

DeBano, L.F. and Letey, J., eds. (1969) *Water-Repellent soils:* Proceedings of the symposium on water repellent soils, May 6-10, 1968, Riverside, CA, Univ. of Calif. Riverside, 354 pp.

Giles, C.H., D'Silva, A.P., and Easton, I.A. (1974) A general treatment and classification of the solute adsorption isotherm. Part II. Experimental interpretation: *J. Colloid Interface Sci.* **47,** 766-778.

Giles, C.H., MacEwan, T.H., Nakhwa, S.N., and Smith, D. (1960) Studies in adsorption. XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids: *J. Chem. Soc.* 3973-3993.

Greenland, D.J. (1965) Interaction between clays and organic compounds in soils. I. Mechanisms of interaction between clays and defined organic compounds: *Soils Fertilizers* **28,** 415-425.

Gschwend, P.M. and Wu, S. (1985) On the constancy of sediment-water partition coefficient of hydrophobic organic pollutants: *Environ. Sci. Technol.* **19,** 90-96.

Hamaker, J.W. and Thompson, J.M. (1972) Adsorption: in *Organic Chemicals in the Soil Environment, Vol. 1,* C.A.I. Goring and J.W. Hamaker, eds., Marcel Dekker, Inc, New York, 49-143.

Hasset, J.J., Means, J.C., Banwart, W.L., and Wood, S.G. (1980) Sorption properties of sediments and energy-related pollutants: *EPA Report 600/3-80-041* U.S. EPA, Springfield, VA.

Hayes, M.H.B., Pick, M.E., and Toms, B.A. (1978) The influence of cation structure on the adsorption of mono- and bipyridinium cations by expanding lattice clay minerals. I. Adsorption by Na^+-montmorillonite: *J. Colloid and Interface Sci.* **65,** 254-265.

Helfferich, F. (1962) *Ion Exchange:* McGraw-Hill Book Co., Inc., New York, 624 pp.

Hendrickx, J.M.H., Dekker, L.W., van Zuilen, E.J., and Boersma, O.H. (1988) Water and solute movement through a water repellent sand soil with grasscover: Contribution for International conference and workshop on validation of flow and transport models for the unsaturated zone, Ruidoso, New Mexico, May 23-26, 1986.

Jaynes, W.F., and Boyd, S.A. (1990) Use of organo-clays for the removal of aromatic gasoline constituents from water: *Agron. Abstr.* **82,** 40.

Jaynes, W.F., Lee, J-F., and Boyd, S.A. (1989) Retention of benzene, toluene and ethylbenzene by organo-clays derived from different clay mineral types: *Agron. Abstr.* **81,** 201.

Jordan, J.W. (1949) Organophilic bentonites. I. Swelling in organic liquids: *J. Phys. Colloid Chem.* **53,** 294-306.

Jordan, J.W. (1963) Organophilic clay-base thickeners: *Clays and Clay Minerals* **10,** 299-308.

Karickhoff, S.W. (1981) Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils: *Chemosphere* **10,** 833-846.

Karickhoff, S.W., Brown, D.S., and Scott, T.A. (1979) Sorption of hydrophobic pollutants on natural sediments: *Water Res.* **13,** 241-248.

Keith, L.H. and Telliard, W.A. (1979) Priority pollutants. I. A perspective view: *Environ. Sci. Technol.* **13,** 416-423.

Kerr, G.T. (1989) Synthetic Zeolites: *Scientific American* **July,** 100-105.

Kolthoff, I.M, and Belcher, R. (1957) *Volumetric analysis, Volume III. Titration methods: Oxidation-reduction reactions:* Interscience Publishers, Inc., New York, 714 pp.

Leo, A., Hansch, H., and Elkins, D. (1971) Partition coefficients and their uses: *Chem. Rev.* **71,** 525-616.

Letey, J., Osborn, J.F., and Valoras, N. (1975) *Soil water repellency and the use of nonionic surfactants:* Contribution No. 154, California Water Resources Center, Univ. of Calif. Davis, 85 pp.

McAtee, J.L. Jr. (1962) Cation exchange of organic compounds on montmorillonite in organic media: *Clays and Clay Minerals* **9,** 444-450.

McAtee, J.L. Jr. (1963) Organic cation exchange on montmorillonite as observed by ultraviolet analysis: *Clays and Clay Minerals* **10,** 153-162.

McAtee, J.L. Jr. and Hackman, J.R. (1964) Exchange equilibria on montmorillonite involving organic cations: *Am. Mineralogist* **49,** 1569-1577.

McBride, M.B., Pinnavaia, T.J., and Mortland, M.M. (1977) Adsorption of aromatic molecules by clays in aqueous suspensions: in *Fate of Pollutants in the Air and Water Environments--Part 1,* I.H. Suffet, ed., Wiley, New York, 145-154.

Ming, D.W. and Dixon, J.B. (1987a) Zeolites: Recent developments in soil mineralogy: in *Transactions of the XIII Congress of the International Society of Soil Science: Symposia Papers,* **V,** 371-382, Hamburg, West Germany, Aug. 13-20, 1986.

Ming, D.W and Dixon, J.B. (1987b) Quantitative determination of clinoptilolite in soils by a cation-exchange capacity method: *Clays and Clay Minerals* **35,** 463-468.

Ming, D.W. and Dixon, J.B. (1988) Occurrence and weathering of zeolites in soil environments: in *Occurrence, Properties, and Utilization of Natural Zeolites,* D. Kalló and H.S. Sherry, eds., Akadémiai Kiadó, Budapest, 699-715.

Ming, D.W. and Mumpton, F.A. (1989) Zeolites in soils: in *Minerals in Soil Environments, 2nd Edition,* J.B. Dixon and S.B. Weed, eds., Soil Sci. Soc. Am., Madison, Wisconsin.

Mingelgrin, U. and Gerstl, Z. (1983) Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils: *J. Environ. Qual.* **12,** 1-11.

Mortland, M.M. (1970) Clay-organic complexes and interactions: *Advan. Agron.* **22,** 75-117.

Mortland, M.M. (1986) Mechanisms of adsorption of nonhumic organic species by clays: in *Interaction of Soil Minerals with Natural Organics and Microbes,* P.M. Huang and M. Schnitzer, eds., Soil Sci. Soc. Am., Madison, Wisconsin, 59-76.

Mortland, M.M., Shaobai, S., and Boyd, S.A. (1986) Clay-organic complexes as adsorbents for phenol and chlorophenols: *Clays and Clay Minerals* **34,** 581-585.

Nelson, D.W., and Sommers, L.E. (1982) Total carbon, organic carbon, and organic matter, in: *Methods of Soil Analysis, Part II, Chemical and Microbiological Properties, 2nd ed.,* A.L. Page, R.H. Miller, and R. Keeney, eds., American Soc. Agronomy, Soil Sci. Soc. Am., Madison, Wisconsin, pp. 539-594.

Newsam, J.M. (1986) The zeolitic cage structure: *Science* **231,** 1093-1099.

Pauling, L. (1967) *The Chemical Bond:* Cornell University Press, Ithaca, New York, 267 pp.

Polemio, M. and Rhoades, J.D. (1977) Determining cation exchange capacity: A new procedure for calcareous and gypsiferous soils: *Soil Sci. Soc. Am. J.* **41,** 524-528.

Rhoades, J.D. (1982) Cation exchange capacity: in *Methods of Soil Analysis, Part II, Chemical and Microbiological Properties, 2nd ed.,* A.L. Page, R.H. Miller, and R. Keeney, eds., American Soc. Agronomy, Soil Sci. Soc. Am., Madison, Wisconsin, pp. 149-158.

Schellenberg, K., Leuenberger, C., and Schwarzenbach, R.P. (1984) Sorption of chlorinated phenols by natural sediments and aquifer materials: *Environ. Sci. Technol.* **18,** 652-657.

Slabaugh, W.H. and Hanson, D.B. (1969) Solvent selectivity by an organoclay complex: *J. Colloid Interface Sci.* **29,** 460-463.

Smith, C.R. (1934) Base-exchange reactions of bentonite and salts of organic bases: *J. Am. Chem. Soc.* **56,** 1561.

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

Stephen, H., and Stephen, T., eds. (1963) *Solubilities of inorganic and organic compounds, Volume I., Part I., Binary systems:* The Macmillan Co., New York, 960 pp.

Stuhl, M.S., Uytterhoeven, J.B., deBock, J., and Huyskens, P.L. (1979) The adsorption of n-aliphatic alcohols from dilute aqueous solutions on RNH3-montmorillonites. II. Interlamellar association of the adsorbate: *Clays and Clay Minerals* **27,** 377-386.

Theng, B.K.G. (1974) *The Chemistry of Clay-Organic Reactions:* John Wiley and Sons, New York, 343 pp.

Theng, B.K.G. (1979) *Formation and Properties of Clay-Polymer Complexes:* Elsevier Scientific Publishing Co., New York, 362 pp.

Toro-Suarez, I., Rao, P.S.C., and Boyd, S.A. (1990) Reduced transport of organic contaminants in modified soils: *Agron. Abstr.* **82,** 49.

Van Dam, J.C., Hendrickx, J.M.H., van Ommen, H.C., Bannink, M.H., van Genuchten, M. Th., and Dekker, L.W. (1990) Water and solute movement in a coarse-textured water-repellent field soil: *J. Hydrology,* (in press).

Verschueren, K. (1983) *Handbook of Environmental Data on Organic Chemicals:* Van Nostrand/Reinhold Press, New York, 659 pp.

Weiss, A. (1963) Mica-type layer silicates with alkyl-ammonium ions: in *Clays and Clay Minerals* **10,** 191-224.

Weiss, A. (1969) Organic derivatives of clay minerals, zeolites, and related minerals, in: *Organic Geochemistry,* G. Eglinton and M.T.J. Murphy, eds., Springer Verlag, Berlin, 737-781.

Wesson, L.G. (1948) *Tables of Electric Dipole Moments:* The Technology Press, Massachussettes Institute of Technology, Cambridge, Mass., 90 pp.

Wilson, J.L. (1988) The need for research: Physical processes--Land; The role of wetting in environmental problems: in *Fundamental Research Directions in Environmental Engineering Conference,* R.G. Luthy and M.J. Small, eds., Proc. Assoc. Env. Eng. Professors, Arlington, Virginia, November 13-15, 1988, Washington, DC, 16-24.

Wilson, J.L., Conrad, S.H., Mason, W.R., Peplinski, W., and Hagan, E. (1990) Laboratory investigation of residual organics from spills, leaks, and the disposal of hazardous wastes in groundwater: *EPA Report 600/6-90/004* U.S. EPA, Ada, Oklahoma, 267 pp.

Wolfe, T.A., Demirel, T., and Baumann, E.R. (1985) Interaction of aliphatic amines with montmorillonite to enhance adsorption of organic pollutants: *Clays and Clay Minerals* **33,** 301-311.

Wolfe, T.A., Demirel, T., and Baumann, E.R. (1986) Adsorption of organic pollutants on montmorillonite treated with amines: *J. Water Poll. Control Fed.* **58,** 68-76.

Wu, S. and Gschwend, P. (1986) Sorption kinetics of hydrophobic organic compounds to natural sediments and soils: *Environ. Sci. Technol.* **20,** 717-725.

APPENDIX A

Abbreviations

AC = Activated Carbon
BDMHDA = Benzyldimethylhexadecylammonium
BTE = Benzene, Toluene, Ethylbenzene
BTEA = Benzyltriethylammonium
BTMA = Benzyltrimethylammonium
CEC = Cation Exchange Capacity
DCB = Dichlorobenzene
DDA = Dodecylammonium
DDDA = Dodecyldiammonium
DODDMA = Dioctadecyldimethylammonium
DDTMA = Dodecyltrimethylammonium
DMBL = Dimethylbenzyllaurelammonium
EHDDMA = Ethylhexadecyldimethylammonium
Eben = Ethylbenzene
GC = Gas Chromatography
HA = Heptylammonium
HDP = Hexadecylpyridinium
HDTMA = Hexadecyltrimethylammonium
HPLC = High Performance Liquid Chromatography
IR = Infrared Spectroscopy
4-MP = 4-Mercaptopyridinium
MPP = Methyl-4-phenylpryidinium
OM = Organic Matter
PA = Propylammonium
PCE = Perchloroethylene (Tetrachloroethylene)
PCP = Pentachlorophenol
Ph = Phenol
PTMA = Phenyltrimethylammonium
SEM = Scanning Electron Microscopy
TCA = 1,1,1-Trichloroethane
TCB = Trichlorobenzene
TCE = Trichloroethylene
TDA = Tetradecylammonium
TDTMA = Tetradecyltrimethylammonium
TEA = Tetraethylammonium
TMA = Tetramethylammonium
TPA = Tetrapropylammonium
XRD = X-ray Diffraction Spectroscopy

APPENDIX B

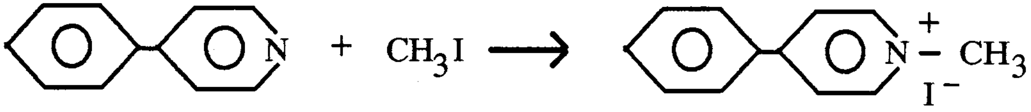
Synthesis and Purity Quantification of Methyl-4-Phenylpyridinium Iodide

Introduction

One of the large organic cations used in this study, methyl-4-phenylpyridinium ion (MPP), is not available commercially. As a result, it was necessary to synthesize this compound in our lab. The iodide salt was synthesized, then its purity determined by a titration for iodide, based on the theoretical concentration of iodide present from the molecular weight of the MPP-I salt. The procedures for the salt synthesis and iodide titration are outlined in this appendix.

MPP-I Synthesis

Methyl-4-phenylpyridinium iodide is easily formed from the reaction of 4-phenylpyridine and methyl iodide, as shown below.



When this reaction is done in acetone, the starting compounds are soluble in the organic liquid, but the final product, (MPP-I), a salt, is insoluble and drops out as a solid precipitate. Reagent grade 4-phenylpyridine was supplied by Sigma Chemical Co., (St. Louis, Missouri). Reagent grade methyl iodide was supplied by Aldrich Chemical Co., (Milwaukee, Wisconsin). The synthesis steps are as follows:

1. Dissolve approximately 25 g (0.16 moles) 4-phenylpyridine in approximately 500 mL acetone. The solid dissolves quite rapidly, usually within a matter of minutes.
2. Add an equi-molar amount of cold (0°C) methyl iodide to the solution. For 25 g 4-phenylpyridine, this corresponds to about 10 mL methyl iodide. Add approximately 1.5 mL excess methyl iodide to the solution. The solution becomes yellow colored almost instantly.
3. Stir the mixture with a magnetic stirrer in a stoppered Erlenmeyer flask for at least 3 hours, during which time the MPP-I precipitates.
4. Pour the solution into a buchner funnel lined with 22 micron filter paper, and rinse the solid over the filter paper with acetone. Dry the solid on the filter paper under suction for approximately 15 minutes.

Using this procedure, we recovered 60-75% of the theoretical maximum mass of MPP-I based on the number of moles of each compound added.

Purity Quantification

An iodide titration modified from procedures outlined in Kolthoff and Belcher (1957, p. 249) was used to quantify the MPP-I purity. The specific procedure used is as follows:

1. Add an aliquot of unknown sample containing at least 10 mg I^- to a 250 mL Erlenmeyer flask. Dilute to 100 mL.
2. Add 5 mL glacial acetic acid.
3. Add 10-20 mL 20% sodium acetate.
4. Add excess 5% bromine water. This requires at least 15 mL bromine water. The solution should change from a light yellow color to a deeper, light orange color resembling diluted bromine water. Let the solution stand 10 minutes.
5. Add 90% formic acid dropwise, swirling after each drop, until the bromine color disappears. This should require only 3-4 drops.
6. Add excess 5% potassium iodide solution. Approximately 5 mL were added for each of these samples. The solution should turn a light yellow color.
7. Add excess dilute sulfuric acid. Approximately 5 mL of 2.9% H_2SO_4 was added to these samples. The solution should turn a deeper yellow color.
8. Titrate with 0.1 N sodium thiosulfate solution. It may be necessary to standardize the thiosulfate solution with a standard potassium iodide solution prior to titrating unknowns. When the solution becomes a very pale yellow color, add approximately 1 mL starch indicator (0.25 g starch per 100 mL water). The solution should turn a dark blue to purple color. Titrate until the solution turns clear and remains clear for a period of approximately 10 full minutes.

Titration Theory and Calculations

The chemical transformations occurring during the titration are as follows: first, iodide is oxidized to iodate ion using bromine. Excess bromine is removed with formic acid. Excess iodide and acid are added to reduce the iodate ion to iodine (I_2). The iodine is then titrated with standard thiosulfate solution in an acidic solution to the endpoint. Each reaction step is shown below.

1. Oxidation of iodide to iodate:

$$I^- + 3Br_2 + 3H_2O \rightarrow IO_3^- + 6Br^- + 6H^+$$

2. Removal of excess bromine:

$$HCOOH + Br_2 \rightarrow CO_2 + 2HBr$$

3. Reduction of iodate to iodine:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

4. Thiosulfate titration:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Since the starch forms the strong purple colored complex with the I_2, when the purple color disappears, the I_2 has been fully titrated.

By this process, six equilivents of thiosulfate are required per mole of iodide. Thus, the equation to calculate iodide mass in unknowns is:

$$\text{Moles } I^- =$$

$$\text{Normality (eq/L) } S_2O_3^{2-} \text{ x } \frac{1 \text{ mole } I^-}{6 \text{ eq } S_2O_3^{2-}} \text{ x mL } S_2O_3^{2-} \text{ titrated x } \frac{1 \text{ L}}{1000 \text{ mL}} \qquad [1]$$

To get the concentration of iodide in the unknown, divide the number of moles I^- by the number of liters of the original unknown aliquot used, for I^- concentration in Moles/L.

Analytical Results

After the MPP-I had been prepared and dried as described earlier, a mass of 121.1 mg product was weighed and dissolved in 100 mL distilled water. Based on the molecular weight of Iodine of 126.9 and the formula weight of MPP-I of 297.14, this represented a theoretical I^- concentration of 0.517 mg/mL. A 20 mL and a 30 mL aliquot of this solution was titrated with standardized 0.104 N sodium thiosulfate solution. Results are shown in Table B-1.

Table B-1. Results of Iodide Titration.

Sample Aliquot	Theoretical I^- conc. (mg/mL)	Theoretical Total I^- (moles)	Volume Thiosulfate Titrated (mL)	Measured Total I^- (moles, Eq. 1)
20 mL	0.517	8.15×10^{-5}	4.90	8.49×10^{-5}
30 mL	0.517	1.22×10^{-4}	6.50	1.13×10^{-4}

From these data, the sample purity was 95.8% or 92.6%, based on results from the 20 mL or 30 mL aliquots, respectively. Because there are errors associated with the titration and solid weighing and solution preparation steps, it is likely that the MPP-I purity was greater than 95%.

APPENDIX C

Characterization of Cation Exchange Properties of Natural Zeolite

Introduction

The substrate used in this study was a natural zeolite mined from a deposit in Tilden, Texas. X-ray diffraction (XRD) analyses confirmed that the bulk sample mineralogy consisted primarily of the zeolite clinoptilolite and smectite. The sample had been pretreated with a pH 5 sodium acetate-acetic acid buffer to remove carbonates (Appendix D).

Before any surface treatments could be performed on this zeolite, it was essential to understand the cation exchange properties of the substrate. This appendix details two laboratory experiments designed to quantify both the total CEC and external (non-zeolitic) CEC of the substrate. It was essential to know not only the total CEC, but also the external CEC, since the large organic cations used to alter the zeolite surface were too large to enter into the internal zeolitic cavities. The method for determining total CEC follows that of Rhoades (1982). The method for determining zeolitic and nonzeolitic CEC follows that of Ming and Dixon (1987b).

Total CEC Determination

The method of total CEC measurement presented by Rhoades (1982) is a slight modification of the method developed by Polemio and Rhoades (1977). The Polemio and Rhoades method is particularly well suited to calcareous and gypsiferous soils, although it is valid for a wide range of soils. Because carbonates had been previously removed from our samples, potential interferences due to carbonate dissolution had already been eliminated. The Polemio and Rhoades method is also preferable to other methods because it eliminates the rinsing step of the saturating solution, a step that may often introduce additional errors to the CEC measurement.

Zeolite samples were analyzed in triplicate, with an additional blank sample, containing no zeolite, in 50-mL polyethylene centrifuge tubes. All extracts were analyzed for sodium using a Varian Corp. (Sunnyvale, California) Model 1200AA atomic absorption spectrophotometer. Standards and dilutions were prepared in the magnesium nitrate extracting solution. All extracts were analyzed for chloride using a mercuric nitrate titrimetric method from the American Public Health Association (1960). Once the sodium and choloride content of each extract had been determined and corrected for the blank, the zeolite CEC was determined using the equation:

$$\mathrm{CEC}\left[\frac{\mathrm{me}}{100\ \mathrm{g}}\right] = \qquad [\text{C-1}]$$

$$\frac{10}{\text{zeolite mass (g)}} \times [(\text{Na conc. in me/L}) \times (\mathrm{DF}_{\mathrm{Na}}) - (\text{Cl conc. in me/L}) \times (\mathrm{DF}_{\mathrm{Cl}}) \times (\mathrm{Na/Cl})_{\mathrm{satsol}}]$$

where DF represents the dilution factor and $(\mathrm{Na/Cl})_{\mathrm{satsol}}$ represents the mass ratio of sodium to chloride in the saturating solution. Sodium in the tube blank was assumed to be due to both residual saturating solution droplets and sodium sorption to the tube. Because the amount of sodium in unknowns due to residual saturating solution is corrected in the CEC calculation, this amount was subtracted from the blank sodium value using the amount of chloride measured in the tube blank and applying the $\mathrm{Na/Cl}_{\mathrm{satsol}}$ ratio. After correcting for the residual saturating solution droplets in the tube blank, it was evident that some sorption to the polyethylene tubes occurred. Reasons for this sorption are not known at this time, however, this remaining amount of sodium was subtracted from all the unknown samples to correct for tube sorption. Results of the analyses are presented in Table C-1.

Table C-1.
Raw Data for Total CEC Measurement.

Sample Number	Zeolite Mass (g)	Total Raw[1] Na Conc. (ppm)	Corrected[2] Na Conc. (ppm)	Corrected Na Conc. (me/L)	Total Raw Cl Conc. (ppm)	Cl Conc. (me/L)
1	4.6020	840	807.2	35.11	124.9	3.52
2	4.2361	790	757.2	32.93	126.8	3.58
3	4.1014	1085	1052.2	45.77	132.7	3.74
4	blank	121.3	0	0	27.3	--

Notes:

1. Total Raw Conc. = Measured Conc. (from AA for Na, or titration for Cl) x Dilution Factor
2. Corrected Conc. = Total Raw Na Conc. for zeolite samples - [Total Raw Na Conc. in Tube Blank - (Total Cl Conc. in Tube Blank x $\mathrm{Na/Cl}_{\mathrm{satsol}}$)]
3. $\mathrm{Na/Cl}_{\mathrm{satsol}}$ = 3.24, determined as a mass ratio by:

$$\frac{5\ \text{moles Na}}{1\ \text{mole Cl}} \times \frac{22.99\ \text{g/mole Na}}{35.45\ \text{g/mole Cl}}$$

Applying the data in Table C-1 to Eq. [C-1] resulted in the measured CEC values, as shown in

Table C-2. Discussion of these results follows the section on internal and external CEC.

Table C-2.
Measured Total CEC Values (Rhoades, 1982, method).

Sample Number	CEC (me/100 g)
1	51.5
2	50.4
3	82.1

Internal and External CEC Determination

The Ming and Dixon (1987b) method of internal and external CEC determination was developed as a method to quantify the amount of clinoptilolite in a soil on the basis of the zeolite mineral's internal CEC. This method requires that carbonates are removed prior to the measurement to avoid interferences. Since carbonates had been previously removed, these potential interferences were eliminated.

The Ming and Dixon method essentially involves a two-step process, one an exchange on the external surface, and a second exchange on the internal zeolite surface. All exchange sites are first saturated with sodium, then all non-zeolitic (external) sites are exchanged with a tert-butylammonium ion, which is too large to enter into the internal zeolitic cavities. Sodium is quantified in these extracts to determine non-zeolitic CEC. Next, sodium ions on the internal zeolitic sites are replaced with ammonium ions, which will enter the zeolitic cavities. Sodium in these extracts is quantified to determine the internal CEC.

As in the total CEC analysis, zeolite samples were analyzed in triplicate in 50-mL polyethylene centrifuge tubes, with an additional tube blank containing no zeolite. Sodium analyses were also performed using atomic absorption spectrophotometry. Standards and dilutions for the external CEC (extracted with tert-butylammonium solution) were prepared in Type I water. Standards and dilutions for the internal CEC (extracted with ammonium acetate) were prepared in ammonium acetate solutions. Sodium concentrations were corrected for the amount of sodium found in the tube blank prior to calculating the CEC. Measured sodium concentrations from these steps are presented in Table C-3.

Table C-3.
Raw Data for Internal and External CEC Measurement.

		External CEC (t-butylam. extract)			Internal CEC (NH_4OAC extract)		
Sample Number	Zeolite Mass (g)	Total Raw[1] Na Conc. (ppm)	Corrected[2] Na Conc. (ppm)	Total Na (me)[3]	Total Raw Na Conc. (ppm)	Corrected Na Conc. (ppm)	Total Na (me)
1	4.2432	278.4	278.0	1.21	312.5	312.5	1.36
2	3.9264	244.7	244.3	1.06	292.0	292.0	1.27
3	2.6025	194.9	194.5	0.846	121.5	121.5	0.528
4	blank	0.40	0	--	0.01	0	--

Notes:

1. Total Raw Conc. = Measured Conc. x Dilution Factor
2. Corrected Conc. = Total Raw Conc. for zeolite samples - Total Raw Conc. in Tube Blank
3. Each extract was a 100 mL volume, so the calculation used was:

$$\text{Total Na (me)} = \text{Corrected Na (ppm)} \times 0.1 \text{ L} \times \frac{1 \text{ eq Na}}{22.99 \text{ g Na}}$$

Note that this assumes a dilute solution, so that ppm Na = mg/L Na.

From these data, the CEC is calculated using Eq. [C-2]:

$$\text{CEC}\left[\frac{\text{me}}{100 \text{ g}}\right] = \frac{\text{Total Na (me)} \times 100}{\text{zeolite mass (g)}} \qquad [C\text{-}2]$$

Applying the data in Table C-3 to Eq. [C-2] results in the measured internal, external, and Total CEC values, as shown in Table C-4.

Table C-4.
Measured Internal, External, and Total CEC (Ming and Dixon, 1987b, method).

Sample Number	Internal CEC (me/100g)	External CEC (me/100g)	Total CEC (me/100g)
1	32.1	28.5	60.6
2	32.3	27.0	59.3
3	20.3	32.5	52.8

Summary and Conclusions

Six different subsamples of the zeolite were analyzed for their cation exchange characteristics. The average CEC of all six samples was 59.4 me/100 g. Minor discrepancies in replicate reproducibility are undoubtedly due to the variety of potential errors inherent to the CEC measurements themselves (many of which are discussed in the text in section IV), and to standard errors in laboratory procedures (subsample representativeness, dilution errors, analytical instrument or procedural errors, and others). Because data from two different methods of CEC determination gave comparable results, it is reasonable to conclude from these data that the total average zeolite CEC is approximately 60 me/100 g. Results of the Ming and Dixon (1987b) method showed an average external CEC of 29.3 me/100 g. For calculations and estimations, an approximate external CEC of 30 me/100 g was assumed.

APPENDIX D

Procedure for Zeolite Surface Modification

As part of this project, a procedure for zeolite surface modification was developed. Although other researchers have developed similar methods, specific differences in substrate properties necessitated the development of this method. Existing surface modification methods were designed for clay alteration, which can require special treatment due to their extremely small particle size and tendancy to flocculate. Our material was neither clay sized nor predominantly clay minerals. Rather, the bulk zeolite material in this study was no more than 40% clay minerals, and was sand sized.

Zeolite surfaces were modified using the exchange of large organic cations onto cation exchange sites. Results of organic cation sorption isotherms to the zeolite were used to refine the treatment procedure. Results of several rinsing steps and subsequent modified surface studies indicated that the modified surface is essentially permanent. The step-by-step treatment procedure is as follows:

1. Raw zeolite from the supplier is subjected to a pH 5 buffered 1.0 M sodium acetate-acetic acid solution to remove carbonates. Approximately 200 g raw zeolite are placed in a 1000 mL beaker, to which approximately 500 mL buffer solution is added. The mixture is allowed to effervesce for at least 24 hours, with occasional stirring. The spent solution is decanted and replaced with fresh buffer. After an additional 24 hours, the spent solution is again decanted, and the zeolite rinsed several times with distilled water and filtered and air dried on a buchner funnel. (Note: Carbonates were initially removed to minimize interferences with the CEC measurement. Carbonate removal continued to provide a more homogeneous sample and to minimize other interferences due to carbonates, particularly carbonate coatings that may have been present on mineral grains).
2. Following carbonate removal, 6.66 g air-dried zeolite are added to a 50 mL Teflon centrifuge tube. An empty tube is tared on a top-loading balance, and the zeolite is added directly to the tube.
3. 20 mL 0.1 M aqueous organic cation solution is added to each tube using either 20 mL pipettes or a buret. This solution concentration, volume, and soil mass results in a number of organic cation equivalents equal to the zeolite external CEC of 30 me/100 g.
4. Shake each tube at a speed of about 50 oscillations per minute on the mechanical shaker for at least 24 hours.
5. Tubes are centrifuged at 7500 rpm for about 15 minutes. The spent supernatent solution is decanted and discarded.
6. Excess organic cation solution is removed with a single distilled water rinse. Ten mL distilled water are added to each tube using a buret, and the mixture is shaken for an additional 15 minutes.
7. The mixture is then filtered and dried on filter paper in a buchner funnel. Each centrifuge tube is thoroughly rinsed with distilled water as the zeolite is transfered to the buchner funnel. The zeolite is rinsed 2-3 more times with distilled water from a squirt bottle as it filters. The material then is allowed to air dry under suction overnight, and is stored in plastic bottles.

APPENDIX E

Procedure for Organic Carbon Analysis

Introduction

To quantify the extent of zeolite surface modification with the large organic cations, one of the methods employed was to measure the organic carbon content of the modified soil. The measured organic carbon content can be compared to the theoretical carbon loading based on the available CEC and carbon molecular weight of the exchanging cation. Such a comparison allows quantification of the effectiveness of the exchange reaction.

The method used was a carbon oxidation in a sealed ampule, followed by quantification of CO_2 generated. A saturated potassium persulfate solution was used as the oxidizing agent. Evolved CO_2 was quantified by infrared absorbance. The carbon mass in unknown samples was determined from a standard plot of IR absorbance units vs. carbon mass in prepared standards. An O.I. Corporation (College Station, Texas) Model 524 Carbon Analyzer was used for all analyses.

The procedure for generating the standard curve and determining the organic carbon content of unknowns is presented below. Volumes of reagents used for the standard curve and unknown samples are slightly different, so both procedures are presented.

Ampule Preparation for Carbon Standards

1. Potassium biphthalate solutions are made at 100 mg/L, 10 mg/L, and 5 mg/L concentrations as organic carbon standards.
2. The appropriate volume of each standard is added to a precombusted ampule to give resultant organic carbon masses between 10 and 500 μg carbon. The volume of each standard added and the associated mass of organic carbon is presented in Table E-1. Each standard concentration was analyzed in triplicate.
3. 1.0 mL saturated potassium persulfate solution (70 g/L) is added to each ampule using a 1 mL pipette.
4. 0.2 mL 10% phosphoric acid is added to each ampule using a 100 μL syringe.
5. Enough distilled water is added to each ampule to bring the total liquid volume up to approximately 6 mL, using pipettes.

Ampule Preparation for Unknown Samples

1. A precombusted ampule is weighed, and a ground mass of sample having an estimated organic carbon mass of approximately 100-400 μg is added to each sample. Typically, about 5-50 mg sample were used.

Table E-1. Volumes of Carbon Standards used and Resultant Carbon Masses for Standard Curve.

Standard Concentration (mg/L)	Sample Volume (mL)	Mass of Organic C (μg)
5	2	10
5	5	25
10	5	50
100	1	100
100	2	200
100	3	300
100	4	400
100	5	500

2. 1.0 mL 10% phosphoric acid is added to each sample using a pipette.
3. 2.0 mL distilled water is added to each ampule using a pipette.
4. 2.0 mL saturated potassium persulfate solution is added to each ampule using a pipette.
5. 2.0 mL distilled water is added to each ampule using a pipette.

Once the reagents are added to the ampules, sample treatment is identical for both the standards and unknowns. The remaining steps are as follows:

1. Each sample is purged of inorganic carbon for approximately 20-30 minutes. The 10% phosphoric acid solution added to each ampule is enough to react with all the inorganic carbon (mainly calcium carbonate) and dissolve it to CO_2 in each sample. This CO_2 is purged from all samples by bubbling pure oxygen through each sample using O.I. Corp. Model 524PS.
2. Each ampule is sealed under a propane-oxygen flame.
3. The ampules are placed in a pressure cooker at 130°C for at least 2 hours (this time includes time for the pressure cooker to warm up to 130°C, which takes about $1\frac{1}{2}$ hours. The samples must be at 130°C for 30 minutes minimum). The potassium persulfate oxides organic carbon after heating, so organic carbon is not oxidized during the purging step, but is completely oxidized only after the ampules are sealed and heated.
4. Once the organic carbon is converted to CO_2 and the ampules cooled, the ampules may be analyzed at any time. The IR analyzer (O.I. Corp. Model 3300) is allowed to warm up for at least 24 hours prior to analyzing samples.
5. The ampules are placed in the breaking assembly of the Analyzer module (O.I. Corp. Model 524D) and sealed with a rubber gasket around the ampule neck. A cut piece of rubber tubing works well as a gasket.
6. The sealed headspace above the tip of each ampule is purged with nitrogen. The nitrogen flow rate is always set at 13 on the module flow meter.
7. After purging, the integrator reading is cleared, and the ampule broken. The purge tube is lowered into the solution and nitrogen bubbled through. The ampule is allowed to purge until the integrator stops, at which point the integrator reading is recorded. Blank samples (containing only reagents) were run with each group of unknowns and standards. Blank sample integrator area was never higher than 7700 units. The blank value is subtracted from

each sample before determining the organic carbon mass.

For the standard curve, integrator area vs. μg organic carbon was plotted. The curve gave a best-fit formula of $\mu\text{g Carbon} = \exp\left[\frac{\text{area} + 140456.5}{80016.6}\right]$, with an $r^2 = 0.9794$. This equation was used to determine the organic carbon mass of unknowns. The organic carbon percent was determined from mass of organic carbon divided by sample mass times 100%. Results of the standard curve are presented in Table E-2, and plotted in Fig. E-1. Integrator areas presented are already corrected for the blank area.

Table E-2. Results of Organic Carbon Standard Curve Analysis.

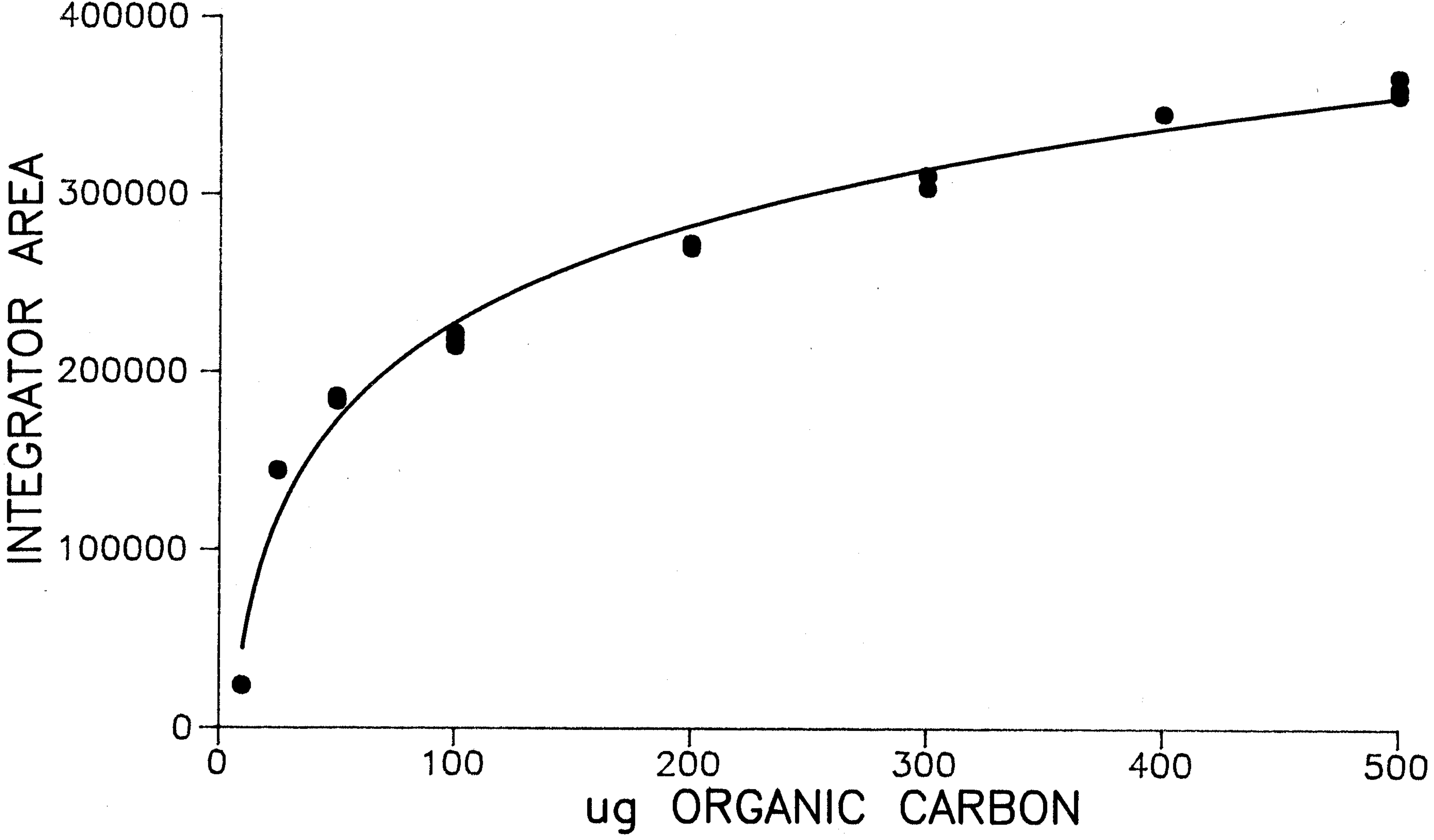
Sample Number	Integrator Area (units)	Organic Carbon Mass (μg)
1A	23693	10
1B	23689	10
1C	23541	10
2A	144541	25
2B	144071	25
2C	143961	25
3A	185872	50
3B	185072	50
3C	183118	50
4A	217685	100
4B	221657	100
4C	213875	100
5A	271390	200
5B	272377	200
5C	269396	200
6A	311072	300
6B	310855	300
6C	303675	300
7A	345838	400
7B	(broken)	
7C	(broken)	
8A	356386	500
8B	360173	500
8C	366527	500

At a minimum, all pipettes were cleaned and rinsed with 5% nitric acid, then air-dried overnight before use. All unknowns were analyzed in duplicate, with duplicate agreement generally very good. Results of unknown samples are presented in Table E-3. Integrator areas have already been corrected for blank values. All values are for zeolites to which a mass of organic cation equal to the zeolite external CEC was added and equilibrated for 24 hours.

Table E-3. Results of Unknown Organic Carbon Analyses.

Sample Contents	Sample Mass (μg)	Integrator Area (units)	Mass Organic Carbon (μg)	Percent Organic Carbon	Average %OC of Duplicates	Theoretical %OC (at CEC)
Natural Zeolite	27800	163361	45	0.16	0.16	--
Natural Zeolite	52900	212842	83	0.16		--
TMA Zeolite	19600	316143	301	1.54	1.57	1.42
TMA Zeolite	16200	303897	258	1.59		1.42
PTMA Zeolite	25000	362181	535	2.14	2.71	3.14
PTMA Zeolite	29800	410082	973	3.27		3.14
HDTMA Zeolite	3100	281774	196	6.32	6.33	6.35
HDTMA Zeolite	4800	316945	304	6.33		6.35
MPP Zeolite	5100	285590	205.3	4.03	3.80	4.14
MPP Zeolite	3200	238742	114.3	3.57		4.14

FIGURE E–1. STANDARD CURVE FOR ORGANIC CARBON ANALYSES



APPENDIX F

Sorption Isotherm Data:

Organic Cations to Natural Zeolite

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

HDTMA TO NATURAL ZEOLITE

Stock Solution Preparation:  216296.00 mg
                               100.00% purity                                  EQUILIBRIUM
                          in      1000 ml                                 --------------------
Stock Solution :  216296.00 mg/l                                   Liq       Liq      Sorbed
Solution Volume = 20.00 ml                                        Conc.      Conc      Conc
C-14 solution:       276.60 mg/l                                (cpm/ml)   (mg/l)   (mg/kg)

***********************************************************
Tube Set:    1                                 Tube 1           132.80      3.50   8564.63
                                                  6.66  g soil
Concentration relative to stock:         0.013

C-14 spike:
   75.00 ul, added to           50.00 ml
                                               Tube 1D         1226.90     32.33   8478.07
Actual sol'n concentration:    2855.52   mg/l     6.66  g soil
Average CPM of solution:     108381.50

***********************************************************
Tube Set:    2                                 Tube 2            99.70     13.58  42700.03
                                                  6.66  g soil
Concentration relative to stock:         0.066

C-14 spike:
   75.00 ul, added to           50.00 ml
                                               Tube 2D          625.20     85.17  42485.04
Actual sol'n concentration:   14232.69   mg/l     6.66  g soil
Average CPM of solution:     104472.50

***********************************************************
Tube Set:    3                                 Tube 3           108.30     30.93  85387.49
                                                  6.66  g soil
Concentration relative to stock:         0.132

C-14 spike:
   75.00 ul, added to           50.00 ml
                                               Tube 3D          798.40    228.04  84795.57
Actual sol'n concentration:   28464.97   mg/l     6.66  g soil
Average CPM of solution:      99658.25

***********************************************************
Tube Set:    4                                 Tube 4           104.10     43.87 128088.22
                                                  6.66  g soil
Concentration relative to stock:         0.197

C-14 spike:
   75.00 ul, added to           50.00 ml
                                               Tube 4D         1013.80    427.22 126937.01
Actual sol'n concentration:   42697.25   mg/l     6.66  g soil
Average CPM of solution:     101321.30

***********************************************************
Tube Set:    5                                 Tube 5           921.80    485.40 169501.87
                                                  6.66  g soil
Concentration relative to stock:         0.263

C-14 spike:
   75.00 ul, added to           50.00 ml
                                               Tube 5D        10997.80   5791.21 153568.50
Actual sol'n concentration:   56929.52   mg/l     6.66  g soil
Average CPM of solution:     108112.00
***********************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

HDTMA TO NATURAL ZEOLITE

Stock Solution Preparation:  216296.00 mg
                                100.00% purity                                     EQUILIBRIUM
                         in       1000 ml                                   --------------------
Stock Solution :  216296.00 mg/l                                     Liq      Liq       Sorbed
Solution Volume = 20.00 ml                                          Conc.     Conc       Conc
C-14 solution:         276.60 mg/l                                (cpm/ml)   (mg/l)    (mg/kg)

************************************************************
Tube Set:     6                                  Tube 6           2588.50   4392.36 414141.73
                                                    6.66  g soil
Concentration relative to stock:          0.658

C-14 spike:
   75.00 ul, added to              50.00 ml
                                                 Tube 6D         37880.10  64277.72 234305.81
Actual sol'n concentration:  142301.55   mg/l       6.66  g soil
Average CPM of solution:      83861.05

************************************************************

Tube Set:     7                                  Tube 7           5458.39   9262.19 621724.38
                                                    6.66  g soil
Concentration relative to stock:          1.000

C-14 spike:
   75.00 ul, added to              50.00 ml
                                                 Tube 7D         55183.50  93639.39 368339.41
Actual sol'n concentration:  216296.41   mg/l       6.66  g soil
Average CPM of solution:      82830.70
************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

MPP TO NATURAL ZEOLITE  --  LIQUID CPM/ML CORRECTED FOR QUENCHING

Stock Solution Preparation:   51072.00 mg
                                100.00% purity                                 EQUILIBRIUM
                         in       1000 ml                                  --------------------
Stock Solution :   51072.00 mg/l                                     Liq     Liq       Sorbed
Solution Volume = 20.00 ml                                          Conc.     Conc      Conc
C-14 solution:        15.50 mg/l                                  (cpm/ml)   (mg/l)   (mg/kg)

************************************************************
Tube Set:    1                                   Tube 1              89.10      8.71   5081.12
                                                    6.66  g soil
Concentration relative to stock:          0.033

C-14 spike:
   75.00 ul, added to            50.00 ml
                                                 Tube 1D             96.90      9.47   5078.83
Actual sol'n concentration:    1700.72   mg/l       6.66  g soil
Average CPM of solution:      17400.00

************************************************************
Tube Set:    2                                   Tube 2              51.80     25.35  25490.63
                                                    6.66  g soil
Concentration relative to stock:          0.167

C-14 spike:
   75.00 ul, added to            50.00 ml
                                                 Tube 2D             59.10     28.92  25479.90
Actual sol'n concentration:    8513.73   mg/l       6.66  g soil
Average CPM of solution:      17400.00

************************************************************
Tube Set:    3                                   Tube 3             305.89    299.25  50219.43
                                                    6.66  g soil
Concentration relative to stock:          0.333

C-14 spike:
   75.00 ul, added to            50.00 ml
                                                 Tube 3D            546.53    534.67  49512.47
Actual sol'n concentration:   17022.32   mg/l       6.66  g soil
Average CPM of solution:      17400.00

************************************************************
Tube Set:    4                                   Tube 4            9460.00  23138.03 116638.39
                                                    3.33  g soil
Concentration relative to stock:          0.833

C-14 spike:
   75.00 ul, added to            50.00 ml
                                                 Tube 4D          13466.70  32937.94  57780.07
Actual sol'n concentration:   42558.32   mg/l       3.33  g soil
Average CPM of solution:      17400.00

************************************************************
Tube Set:    5                                   Tube 5           11836.80  34743.06 122774.12
                                                    2.66  g soil
Concentration relative to stock:          1.000

C-14 spike:
   75.00 ul, added to            50.00 ml
                                                 Tube 5D          16923.30  49672.83  10520.28
Actual sol'n concentration:   51072.02   mg/l       2.66  g soil
Average CPM of solution:      17400.00
************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

MPP TO NATURAL ZEOLITE  --  LIQUID CPM/ML CORRECTED FOR QUENCHING

Stock Solution Preparation:  51072.00 mg
                               100.00% purity                                EQUILIBRIUM
                         in      1000 ml                                 --------------------
Stock Solution :  51072.00 mg/l                                  Liq        Liq      Sorbed
Solution Volume = 20.00 ml                                       Conc.      Conc      Conc
C-14 solution:          15.50 mg/l                             (cpm/ml)    (mg/l)   (mg/kg)

************************************************************
Tube Set:    6                                 Tube 6         1717.20    2520.14  69116.76
                                                  6.66  g soil
Concentration relative to stock:         0.500

C-14 spike:
   75.00 ul, added to           50.00 ml
                                               Tube 6D        2571.40    3773.75  65352.16
Actual sol'n concentration:  25536.02   mg/l      6.66  g soil
Average CPM of solution:     17400.00

************************************************************

Tube Set:    7                                 Tube 7         2938.50    4312.51  89300.96
                                                  6.66  g soil
Concentration relative to stock:         0.667

C-14 spike:
   75.00 ul, added to           50.00 ml
                                               Tube 7D        3984.10    5847.02  84692.82
Actual sol'n concentration:  34049.73   mg/l      6.66  g soil
Average CPM of solution:     17400.00
************************************************************
```

RAW DATA FOR MPP SORPTION TO NATURAL ZEOLITE

MEASURED C14 CPM/ML AND QIP NUMBERS--NOT CORRECTED FOR QUENCHING

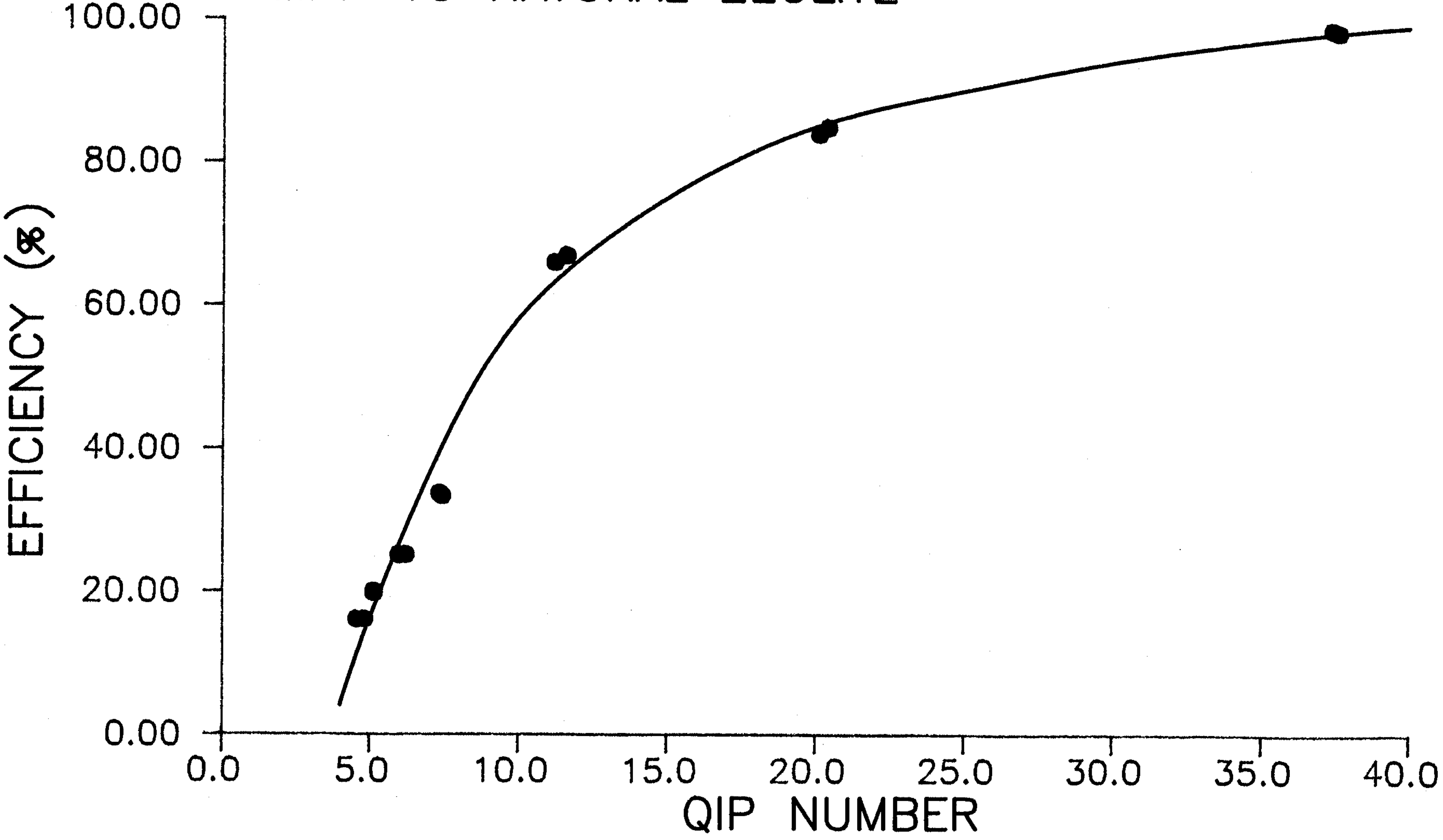
SAMPLE TUBE NUMBER	MEASURED CPM/ML	MEASURED QIP NUMBER	MEASURED EFFECIENCY (%) (FIGURE E-1)	CORRECTED CPM/ML
1	89.10	54.00	100	89.1
1D	96.90	47.80	100	96.9
2	51.80	67.20	100	51.8
2D	59.10	59.30	100	59.1
3	249.30	17.70	81.5	305.89
3D	409.90	15.10	75	546.53
4	1229.80	4.69	13	9460
4D	1616.00	4.55	12	13466.7
5	1124.50	4.41	9.5	11836.8
5D	1523.10	4.12	9	16923.3
6	729.80	7.62	42.5	1717.2
6D	900.40	6.81	35	2571.4
7	793.40	5.90	27	2938.5
7D	976.10	5.64	24.5	3984.1

QUENCH CURVE--MPP TO NATURAL ZEOLITE
DATA TAKEN FROM 1/9/90 EXPERIMENTAL RUN

THEORETICAL CPM/ML = 17400
(BASED ON A 75 uL ADDITION OF PRIMARY STANDARD WITH 5.83 uCi/ML TO EACH 50 ML SOLUTION)

SAMPLE NUMBER	OBSERVED CPM/ML	QIP NUMBER	COUNTING EFFICIENCY (%)
M-1	17127.7	37.4	98.44
M-1D	17068	37.6	98.09
M-2	14750	20.4	84.77
M-2D	14582.9	20.1	83.81
M-3	11627.9	11.6	66.83
M-3D	11466.1	11.2	65.90
M-4	5792.91	7.42	33.29
M-4D	5850.58	7.33	33.62
M-5	4352.67	5.97	25.02
M-5D	4363.47	6.2	25.08
M-6	3428.6	5.13	19.70
M-6D	3464.9	5.13	19.91
M-7	2779.2	4.56	15.97
M-7D	2787.8	4.82	16.02

FIGURE F—1. QUENCH CURVE FOR MPP TO NATURAL ZEOLITE



APPENDIX G

Surface Stability Data

LOTUS SPREADSHEET FOR EQUILIBRIUM ORGANIC CATION
DESORPTION FROM ZEOLITES IN VARIOUS SOLUTIONS

MASS OF TREATED ZEOLITE USED FOR ALL EXPERIMENTS: 5.00 g
SOLUTION VOLUME USED IN ALL EXPERIMENTS: 10.0 ml

TOTAL INITIAL C-14 cpm ON TREATED ZEOLITES:
HDTMA: 1005706.00
MPP: 834345.15

		HDTMA ZEOLITE			
SOLUTION COMPOSITION	TIME (hrs.)	LIQUID cpm/ml	TOTAL LIQUID cpm	CATION % REMOVED	CATION % REMAINING
pH 3.02	4	786.50	7865.00	0.78	99.22
	4	268.10	2681.00	0.27	99.73
	8	246.00	2460.00	0.24	99.76
	8	222.00	2220.00	0.22	99.78
	24	270.50	2705.00	0.27	99.73
	24	296.30	2963.00	0.29	99.71
	48	289.10	2891.00	0.29	99.71
	48	311.40	3114.00	0.31	99.69
	72	306.30	3063.00	0.30	99.70
	72	321.00	3210.00	0.32	99.68
pH 6.95	4	338.10	3381.00	0.34	99.66
	4	356.70	3567.00	0.35	99.65
	8	334.20	3342.00	0.33	99.67
	8	376.20	3762.00	0.37	99.63
	24	466.70	4667.00	0.46	99.54
	24	434.50	4345.00	0.43	99.57
	48	342.98	3429.80	0.34	99.66
	48	460.30	4603.00	0.46	99.54
	72	308.20	3082.00	0.31	99.69
	72	412.50	4125.00	0.41	99.59
pH 8.12	4	345.50	3455.00	0.34	99.66
	4	364.40	3644.00	0.36	99.64
	8	335.10	3351.00	0.33	99.67
	8	366.60	3666.00	0.36	99.64
	24	448.10	4481.00	0.45	99.55
	24	470.80	4708.00	0.47	99.53
	48	394.70	3947.00	0.39	99.61
	48	382.60	3826.00	0.38	99.62
	72	379.50	3795.00	0.38	99.62
	72	389.00	3890.00	0.39	99.61
pH 9.85	4	550.70	5507.00	0.55	99.45
	4	409.60	4096.00	0.41	99.59
	8	405.60	4056.00	0.40	99.60
	8	448.60	4486.00	0.45	99.55
	24	444.60	4446.00	0.44	99.56
	24	530.20	5302.00	0.53	99.47
	48	409.60	4096.00	0.41	99.59
	48	401.40	4014.00	0.40	99.60
	72	431.50	4315.00	0.43	99.57
	72	358.10	3581.00	0.36	99.64
DISTILLED WATER	4	676.90	6769.00	0.67	99.33
	4	576.20	5762.00	0.57	99.43
	8	502.90	5029.00	0.50	99.50
	8	412.70	4127.00	0.41	99.59
	24	560.00	5600.00	0.56	99.44
	24	394.90	3949.00	0.39	99.61
	48	467.10	4671.00	0.46	99.54
	48	497.10	4971.00	0.49	99.51
	72	505.80	5058.00	0.50	99.50
	72	367.80	3678.00	0.37	99.63

LOTUS SPREADSHEET FOR EQUILIBRIUM ORGANIC CATION
DESORPTION FROM ZEOLITES IN VARIOUS SOLUTIONS

MASS OF TREATED ZEOLITE USED FOR ALL EXPERIMENTS: 5.00 g
SOLUTION VOLUME USED IN ALL EXPERIMENTS: 10.0 ml

TOTAL INITIAL C-14 cpm ON TREATED ZEOLITES:

HDTMA:	1005706.00
MPP:	834345.15

		HDTMA ZEOLITE			
SOLUTION COMPOSITION	TIME (hrs.)	LIQUID cpm/ml	TOTAL LIQUID cpm	CATION % REMOVED	CATION % REMAINING
SOLTROL	4	85.50	855.00	0.09	99.91
	4	80.00	800.00	0.08	99.92
	8	68.90	689.00	0.07	99.93
	8	60.90	609.00	0.06	99.94
	24	50.10	501.00	0.05	99.95
	24	77.40	774.00	0.08	99.92
	48	70.60	706.00	0.07	99.93
	48	72.30	723.00	0.07	99.93
	72	55.00	550.00	0.05	99.95
	72	58.80	588.00	0.06	99.94
METHANOL	4	8425.05	84250.50	8.38	91.62
	4	10528.06	105280.60	10.47	89.53
	8	7916.21	79162.10	7.87	92.13
	8	9788.75	97887.50	9.73	90.27
	24	8537.95	85379.50	8.49	91.51
	24	10052.60	100526.00	10.00	90.00
	48	9378.69	93786.90	9.33	90.67
	48	8113.56	81135.60	8.07	91.93
	72	6291.35	62913.50	6.26	93.74
	72	9173.00	91730.00	9.12	90.88
BENZENE	4	294.80	2948.00	0.29	99.71
	4	162.40	1624.00	0.16	99.84
	8	119.40	1194.00	0.12	99.88
	8	116.30	1163.00	0.12	99.88
	24	142.90	1429.00	0.14	99.86
	24	193.70	1937.00	0.19	99.81
	48	1721.40	17214.00	1.71	98.29
	48	221.80	2218.00	0.22	99.78
	72	115.90	1159.00	0.12	99.88
	72	153.10	1531.00	0.15	99.85
0.1 M TMA	4	803.50	8035.00	0.80	99.20
	4	813.70	8137.00	0.81	99.19
	8	913.10	9131.00	0.91	99.09
	8	924.20	9242.00	0.92	99.08
	24	1032.00	10320.00	1.03	98.97
	24	978.90	9789.00	0.97	99.03
	48	1056.70	10567.00	1.05	98.95
	48	1080.70	10807.00	1.07	98.93
	72	1092.30	10923.00	1.09	98.91
	72	1176.40	11764.00	1.17	98.83
1.0 M TMA	4	1558.70	15587.00	1.55	98.45
	4	1485.30	14853.00	1.48	98.52
	8	1788.90	17889.00	1.78	98.22
	8	1664.30	16643.00	1.65	98.35
	24	2189.20	21892.00	2.18	97.82
	24	1908.30	19083.00	1.90	98.10
	48	2228.10	22281.00	2.22	97.78
	48	2002.40	20024.00	1.99	98.01
	72	2480.80	24808.00	2.47	97.53
	72	2181.30	21813.00	2.17	97.83

LOTUS SPREADSHEET FOR EQUILIBRIUM ORGANIC CATION
DESORPTION FROM ZEOLITES IN VARIOUS SOLUTIONS

MASS OF TREATED ZEOLITE USED FOR ALL EXPERIMENTS: 5.00 g
SOLUTION VOLUME USED IN ALL EXPERIMENTS: 10.0 ml

TOTAL INITIAL C-14 cpm ON TREATED ZEOLITES:
HDTMA: 1005706.00
MPP: 834345.15

		HDTMA ZEOLITE			
SOLUTION COMPOSITION	TIME (hrs.)	LIQUID cpm/ml	TOTAL LIQUID cpm	CATION % REMOVED	CATION % REMAINING
0.1 M PTMA	4	667.20	6672.00	0.66	99.34
	4	621.60	6216.00	0.62	99.38
	8	756.00	7560.00	0.75	99.25
	8	685.30	6853.00	0.68	99.32
	24	715.70	7157.00	0.71	99.29
	24	676.60	6766.00	0.67	99.33
	48	719.80	7198.00	0.72	99.28
	48	668.70	6687.00	0.66	99.34
	72	741.40	7414.00	0.74	99.26
	72	714.10	7141.00	0.71	99.29
1.0 M PTMA	4	29967.10	299671.00	29.80	70.20
	4	32264.80	322648.00	32.08	67.92
	8	32379.80	323798.00	32.20	67.80
	8	34920.80	349208.00	34.72	65.28
	24	31677.10	316771.00	31.50	68.50
	24	34305.90	343059.00	34.11	65.89
	48	30392.40	303924.00	30.22	69.78
	48	33525.80	335258.00	33.34	66.66
	72	29989.50	299895.00	29.82	70.18
	72	32794.20	327942.00	32.61	67.39
0.15 M HDTMA	4	-	-	-	-
	4	-	-	-	-
	8	-	-	-	-
	8	-	-	-	-
	24	-	-	-	-
	24	-	-	-	-
	48	-	-	-	-
	48	-	-	-	-
	72	-	-	-	-
	72	-	-	-	-
0.15 M MPP	4	683.50	6835.00	0.68	99.32
	4	736.80	7368.00	0.73	99.27
	8	885.50	8855.00	0.88	99.12
	8	948.00	9480.00	0.94	99.06
	24	1018.50	10185.00	1.01	98.99
	24	1108.80	11088.00	1.10	98.90
	48	1217.50	12175.00	1.21	98.79
	48	1084.60	10846.00	1.08	98.92
	72	1189.30	11893.00	1.18	98.82
	72	1363.00	13630.00	1.36	98.64
0.01 M CsCl	4	376.20	3762.00	0.37	99.63
	4	437.40	4374.00	0.43	99.57
	8	428.20	4282.00	0.43	99.57
	8	429.90	4299.00	0.43	99.57
	24	402.50	4025.00	0.40	99.60
	24	435.10	4351.00	0.43	99.57
	48	441.20	4412.00	0.44	99.56
	48	437.10	4371.00	0.43	99.57
	72	438.80	4388.00	0.44	99.56
	72	474.20	4742.00	0.47	99.53

LOTUS SPREADSHEET FOR EQUILIBRIUM ORGANIC CATION
DESORPTION FROM ZEOLITES IN VARIOUS SOLUTIONS

MASS OF TREATED ZEOLITE USED FOR ALL EXPERIMENTS: 5.00 g
SOLUTION VOLUME USED IN ALL EXPERIMENTS: 10.0 ml

TOTAL INITIAL C-14 cpm ON TREATED ZEOLITES:
HDTMA: 1005706.00
MPP: 834345.15

		HDTMA ZEOLITE			
SOLUTION COMPOSITION	TIME (hrs.)	LIQUID cpm/ml	TOTAL LIQUID cpm	CATION % REMOVED	CATION % REMAINING
0.1 M CsCl	4	359.10	3591.00	0.36	99.64
	4	359.90	3599.00	0.36	99.64
	8	403.60	4036.00	0.40	99.60
	8	397.60	3976.00	0.40	99.60
	24	424.10	4241.00	0.42	99.58
	24	448.50	4485.00	0.45	99.55
	48	448.60	4486.00	0.45	99.55
	48	470.80	4708.00	0.47	99.53
	72	326.10	3261.00	0.32	99.68
	72	471.90	4719.00	0.47	99.53
1.0 M CsCl	4	776.10	7761.00	0.77	99.23
	4	767.10	7671.00	0.76	99.24
	8	833.60	8336.00	0.83	99.17
	8	865.90	8659.00	0.86	99.14
	24	885.50	8855.00	0.88	99.12
	24	847.00	8470.00	0.84	99.16
	48	882.30	8823.00	0.88	99.12
	48	893.30	8933.00	0.89	99.11
	72	967.90	9679.00	0.96	99.04
	72	976.40	9764.00	0.97	99.03
0.005 M CaCl2	4	415.10	4151.00	0.41	99.59
	4	394.00	3940.00	0.39	99.61
	8	484.40	4844.00	0.48	99.52
	8	448.40	4484.00	0.45	99.55
	24	480.60	4806.00	0.48	99.52
	24	422.00	4220.00	0.42	99.58
	48	464.90	4649.00	0.46	99.54
	48	405.70	4057.00	0.40	99.60
	72	522.70	5227.00	0.52	99.48
	72	401.50	4015.00	0.40	99.60

LOTUS SPREADSHEET FOR EQUILIBRIUM ORGANIC CATION
DESORPTION FROM ZEOLITES IN VARIOUS SOLUTIONS

MASS OF TREATED ZEOLITE USED FOR ALL EXPERIMENTS: 5.00 g
SOLUTION VOLUME USED IN ALL EXPERIMENTS: 10.0 ml

TOTAL INITIAL C-14 cpm ON TREATED ZEOLITES:
HDTMA: 1005706.00
MPP: 834345.15

		MPP ZEOLITE			
SOLUTION COMPOSITION	TIME (hrs.)	LIQUID cpm/ml	TOTAL LIQUID cpm	CATION % REMOVED	CATION % REMAINING
pH 3.02	4	2274.50	22745.00	2.73	97.27
	4	2262.10	22621.00	2.71	97.29
	8	2218.20	22182.00	2.66	97.34
	8	2227.60	22276.00	2.67	97.33
	24	2177.30	21773.00	2.61	97.39
	24	2124.80	21248.00	2.55	97.45
	48	2207.60	22076.00	2.65	97.35
	48	2160.40	21604.00	2.59	97.41
	72	2275.30	22753.00	2.73	97.27
	72	2332.00	23320.00	2.80	97.20
pH 6.95	4	1298.30	12983.00	1.56	98.44
	4	1330.20	13302.00	1.59	98.41
	8	1284.10	12841.00	1.54	98.46
	8	1275.50	12755.00	1.53	98.47
	24	1134.80	11348.00	1.36	98.64
	24	1115.20	11152.00	1.34	98.66
	48	1026.70	10267.00	1.23	98.77
	48	1047.10	10471.00	1.25	98.75
	72	1086.90	10869.00	1.30	98.70
	72	1149.30	11493.00	1.38	98.62
pH 8.12	4	1319.10	13191.00	1.58	98.42
	4	1335.70	13357.00	1.60	98.40
	8	1380.60	13806.00	1.65	98.35
	8	1380.50	13805.00	1.65	98.35
	24	1272.30	12723.00	1.52	98.48
	24	1283.30	12833.00	1.54	98.46
	48	1236.90	12369.00	1.48	98.52
	48	1320.30	13203.00	1.58	98.42
	72	1223.80	12238.00	1.47	98.53
	72	1257.50	12575.00	1.51	98.49
pH 9.85	4	886.10	8861.00	1.06	98.94
	4	873.40	8734.00	1.05	98.95
	8	896.80	8968.00	1.07	98.93
	8	892.60	8926.00	1.07	98.93
	24	803.40	8034.00	0.96	99.04
	24	813.20	8132.00	0.97	99.03
	48	774.70	7747.00	0.93	99.07
	48	844.50	8445.00	1.01	98.99
	72	890.90	8909.00	1.07	98.93
	72	933.10	9331.00	1.12	98.88
DISTILLED WATER	4	367.00	3670.00	0.44	99.56
	4	360.50	3605.00	0.43	99.57
	8	401.10	4011.00	0.48	99.52
	8	389.90	3899.00	0.47	99.53
	24	440.10	4401.00	0.53	99.47
	24	426.50	4265.00	0.51	99.49
	48	507.20	5072.00	0.61	99.39
	48	474.60	4746.00	0.57	99.43
	72	539.10	5391.00	0.65	99.35
	72	480.70	4807.00	0.58	99.42

LOTUS SPREADSHEET FOR EQUILIBRIUM ORGANIC CATION DESORPTION FROM ZEOLITES IN VARIOUS SOLUTIONS

MASS OF TREATED ZEOLITE USED FOR ALL EXPERIMENTS: 5.00 g
SOLUTION VOLUME USED IN ALL EXPERIMENTS: 10.0 ml

TOTAL INITIAL C-14 cpm ON TREATED ZEOLITES:
HDTMA: 1005706.00
MPP: 834345.15

		MPP ZEOLITE			
SOLUTION COMPOSITION	TIME (hrs.)	LIQUID cpm/ml	TOTAL LIQUID cpm	CATION % REMOVED	CATION % REMAINING
SOLTROL	4	37.10	371.00	0.04	99.96
	4	40.60	406.00	0.05	99.95
	8	33.70	337.00	0.04	99.96
	8	41.00	410.00	0.05	99.95
	24	35.10	351.00	0.04	99.96
	24	40.70	407.00	0.05	99.95
	48	40.60	406.00	0.05	99.95
	48	40.50	405.00	0.05	99.95
	72	35.80	358.00	0.04	99.96
	72	47.20	472.00	0.06	99.94
METHANOL	4	194.60	1946.00	0.23	99.77
	4	207.30	2073.00	0.25	99.75
	8	195.90	1959.00	0.23	99.77
	8	209.80	2098.00	0.25	99.75
	24	200.80	2008.00	0.24	99.76
	24	211.00	2110.00	0.25	99.75
	48	213.20	2132.00	0.26	99.74
	48	225.80	2258.00	0.27	99.73
	72	231.00	2310.00	0.28	99.72
	72	219.10	2191.00	0.26	99.74
BENZENE	4	100.10	1001.00	0.12	99.88
	4	54.70	547.00	0.07	99.93
	8	48.30	483.00	0.06	99.94
	8	47.90	479.00	0.06	99.94
	24	42.70	427.00	0.05	99.95
	24	55.40	554.00	0.07	99.93
	48	50.90	509.00	0.06	99.94
	48	56.90	569.00	0.07	99.93
	72	54.00	540.00	0.06	99.94
	72	54.00	540.00	0.06	99.94
0.1 M TMA	4	4968.98	49689.80	5.96	94.04
	4	4982.07	49820.70	5.97	94.03
	8	5209.77	52097.70	6.24	93.76
	8	5352.14	53521.40	6.41	93.59
	24	4694.95	46949.50	5.63	94.37
	24	4700.47	47004.70	5.63	94.37
	48	4817.21	48172.10	5.77	94.23
	48	4844.43	48444.30	5.81	94.19
	72	4696.01	46960.10	5.63	94.37
	72	4411.36	44113.60	5.29	94.71
1.0 M TMA	4	11999.40	119994.00	14.38	85.62
	4	12203.00	122030.00	14.63	85.37
	8	12579.50	125795.00	15.08	84.92
	8	12763.30	127633.00	15.30	84.70
	24	11883.00	118830.00	14.24	85.76
	24	12021.30	120213.00	14.41	85.59
	48	11012.30	110123.00	13.20	86.80
	48	11803.50	118035.00	14.15	85.85
	72	11285.00	112850.00	13.53	86.47
	72	11386.60	113866.00	13.65	86.35

LOTUS SPREADSHEET FOR EQUILIBRIUM ORGANIC CATION DESORPTION FROM ZEOLITES IN VARIOUS SOLUTIONS

MASS OF TREATED ZEOLITE USED FOR ALL EXPERIMENTS:	5.00 g
SOLUTION VOLUME USED IN ALL EXPERIMENTS:	10.0 ml

TOTAL INITIAL C-14 cpm ON TREATED ZEOLITES:

HDTMA:	1005706.00
MPP:	834345.15

		MPP ZEOLITE			
SOLUTION COMPOSITION	TIME (hrs.)	LIQUID cpm/ml	TOTAL LIQUID cpm	CATION % REMOVED	CATION % REMAINING
0.1 M PTMA	4	1467.10	14671.00	1.76	98.24
	4	1467.80	14678.00	1.76	98.24
	8	1429.20	14292.00	1.71	98.29
	8	1443.50	14435.00	1.73	98.27
	24	1428.10	14281.00	1.71	98.29
	24	1386.30	13863.00	1.66	98.34
	48	1360.40	13604.00	1.63	98.37
	48	1350.90	13509.00	1.62	98.38
	72	1415.10	14151.00	1.70	98.30
	72	1390.60	13906.00	1.67	98.33
1.0 M PTMA	4	27122.90	271229.00	32.51	67.49
	4	27058.70	270587.00	32.43	67.57
	8	27001.30	270013.00	32.36	67.64
	8	26221.50	262215.00	31.43	68.57
	24	25873.50	258735.00	31.01	68.99
	24	26889.90	268899.00	32.23	67.77
	48	25081.20	250812.00	30.06	69.94
	48	25480.80	254808.00	30.54	69.46
	72	25209.40	252094.00	30.21	69.79
	72	25517.80	255178.00	30.58	69.42
0.15 M HDTMA	4	11873.50	118735.00	14.23	85.77
	4	12993.50	129935.00	15.57	84.43
	8	14286.30	142863.00	17.12	82.88
	8	15166.20	151662.00	18.18	81.82
	24	17616.20	176162.00	21.11	78.89
	24	18123.50	181235.00	21.72	78.28
	48	18698.60	186986.00	22.41	77.59
	48	18972.00	189720.00	22.74	77.26
	72	19254.30	192543.00	23.08	76.92
	72	19794.00	197940.00	23.72	76.28
0.15 M MPP	4	-	-	-	-
	4	-	-	-	-
	8	-	-	-	-
	8	-	-	-	-
	24	-	-	-	-
	24	-	-	-	-
	48	-	-	-	-
	48	-	-	-	-
	72	-	-	-	-
	72	-	-	-	-
0.01 M CsCl	4	862.40	8624.00	1.03	98.97
	4	871.50	8715.00	1.04	98.96
	8	841.30	8413.00	1.01	98.99
	8	843.10	8431.00	1.01	98.99
	24	827.40	8274.00	0.99	99.01
	24	838.10	8381.00	1.00	99.00
	48	817.50	8175.00	0.98	99.02
	48	865.00	8650.00	1.04	98.96
	72	866.00	8660.00	1.04	98.96
	72	926.10	9261.00	1.11	98.89

LOTUS SPREADSHEET FOR EQUILIBRIUM ORGANIC CATION
DESORPTION FROM ZEOLITES IN VARIOUS SOLUTIONS

MASS OF TREATED ZEOLITE USED FOR ALL EXPERIMENTS: 5.00 g
SOLUTION VOLUME USED IN ALL EXPERIMENTS: 10.0 ml

TOTAL INITIAL C-14 cpm ON TREATED ZEOLITES:
HDTMA: 1005706.00
MPP: 834345.15

		MPP ZEOLITE			
SOLUTION COMPOSITION	TIME (hrs.)	LIQUID cpm/ml	TOTAL LIQUID cpm	CATION % REMOVED	CATION % REMAINING
0.1 M CsCl	4	2676.10	26761.00	3.21	96.79
	4	2674.10	26741.00	3.21	96.79
	8	2515.80	25158.00	3.02	96.98
	8	2631.10	26311.00	3.15	96.85
	24	2389.20	23892.00	2.86	97.14
	24	2409.20	24092.00	2.89	97.11
	48	2475.40	24754.00	2.97	97.03
	48	2340.20	23402.00	2.80	97.20
	72	2607.80	26078.00	3.13	96.87
	72	2631.60	26316.00	3.15	96.85
1.0 M CsCl	4	8241.56	82415.60	9.88	90.12
	4	8333.68	83336.80	9.99	90.01
	8	8115.01	81150.10	9.73	90.27
	8	8241.77	82417.70	9.88	90.12
	24	7890.34	78903.40	9.46	90.54
	24	7950.79	79507.90	9.53	90.47
	48	7924.36	79243.60	9.50	90.50
	48	7736.94	77369.40	9.27	90.73
	72	7602.09	76020.90	9.11	90.89
	72	7732.24	77322.40	9.27	90.73
0.005 M CaCl2	4	879.60	8796.00	1.05	98.95
	4	875.10	8751.00	1.05	98.95
	8	876.50	8765.00	1.05	98.95
	8	887.20	8872.00	1.06	98.94
	24	844.90	8449.00	1.01	98.99
	24	850.00	8500.00	1.02	98.98
	48	839.00	8390.00	1.01	98.99
	48	843.60	8436.00	1.01	98.99
	72	877.70	8777.00	1.05	98.95
	72	876.40	8764.00	1.05	98.95

APPENDIX H

Sorption Isotherm Data:

Organic Solutes to Surface-Altered Zeolites

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: EBEN, METHANOL, HDTMA--BLANK CORRECTED

EQUILIBRATION TIME: 8 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 94870.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	5986.00	12.85			
1-SAMPLE	5528.00		11.65	12.81	6.15
1-SAMPLE	5433.00		11.45	13.01	7.29
2-STD (BLANK)	15017.00	31.66			
2-SAMPLE	14086.00		29.70	13.34	10.47
2-SAMPLE	14053.00		29.63	12.93	10.51
3-STD (BLANK)	34092.00	71.87			
3-SAMPLE	34829.00		73.42	13.50	-8.39
3-SAMPLE	34361.00		72.44	13.06	-2.96
4-STD (BLANK)	50649.00	106.78			
4-SAMPLE	51076.00		107.68	13.03	-4.69
4-SAMPLE	52127.00		109.89	13.22	-16.48
5-STD (BLANK)	74658.00	168.18			
5-SAMPLE	70929.00		149.53	13.36	99.69
5-SAMPLE	80760.00		170.25	13.02	-10.79

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: EBEN, METHANOL, MPP--BLANK CORRECTED

EQUILIBRATION TIME: 48 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 94870.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	7934.00	16.73			
1-SAMPLE	7383.00		15.56	13.01	6.04
1-SAMPLE	6907.00		14.56	13.06	11.31
2-STD (BLANK)	18188.00	38.34			
2-SAMPLE	18838.00		39.71	12.91	-7.08
2-SAMPLE	16107.00		33.96	13.43	23.57

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 151927.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
3-STD (BLANK)	59343.00	78.01			
3-SAMPLE	57100.00		75.17	13.46	15.32
3-SAMPLE	58134.00		76.53	13.62	8.09
4-STD (BLANK)	72397.00	95.30			
4-SAMPLE	73251.00		96.43	13.14	-5.91
4-SAMPLE	72760.00		95.78	13.57	-2.59
5-STD (BLANK)	116563.00	153.45			
5-SAMPLE	111212.00		146.40	13.83	38.97
5-SAMPLE	109947.00		144.74	13.32	46.40

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: EBEN, METHANOL, NATURAL--BLANK CORRECTED

EQUILIBRATION TIME: 24 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 94870.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	6371.00	12.85			
1-SAMPLE	6015.00		12.68	13.10	0.91
1-SAMPLE	6085.00		12.83	13.02	0.14
2-STD (BLANK)	15017.00	31.66			
2-SAMPLE	12917.00		27.23	12.92	22.88
2-SAMPLE	12289.00		25.91	13.08	30.09
3-STD (BLANK)	34092.00	71.87			
3-SAMPLE	31223.00		65.82	13.53	32.73
3-SAMPLE	31550.00		66.51	12.97	27.80
4-STD (BLANK)	43359.00	91.41			
4-SAMPLE	44558.00		93.93	13.60	-13.75
4-SAMPLE	39156.00		82.55	13.67	48.45

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 151927.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
5-STD (BLANK)	76790.00	101.09			
5-SAMPLE	73951.00		97.35	13.46	20.12
5-SAMPLE	73347.00		96.56	13.87	25.15
6-STD (BLANK)	115282.00	151.76			
6-SAMPLE	110736.00		145.78	13.32	31.89
6-SAMPLE	110952.00		146.06	13.54	30.87

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: EBEN, WATER, HDTMA--BLANK CORRECTED

EQUILIBRATION TIME: 8 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 70753.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	548.00	1.55			
1-SAMPLE	296.00		0.84	12.99	3.70
1-SAMPLE	228.00		0.64	13.24	4.79
2-STD (BLANK)	4882.00	13.80			
2-SAMPLE	698.00		1.97	12.58	59.51
2-SAMPLE	511.00		1.44	13.34	65.93
3-STD (BLANK)	3723.00	10.52			
3-SAMPLE	455.00		1.29	12.75	47.11
3-SAMPLE	360.00		1.02	13.47	51.22
4-STD (BLANK)	41045.00	116.02			
4-SAMPLE	2796.00		7.90	13.33	576.49
4-SAMPLE	2714.00		7.67	13.16	570.36
5-STD (BLANK)	29945.00	84.65			
5-SAMPLE	2060.00		5.82	12.90	406.73
5-SAMPLE	2164.00		6.12	13.40	420.92
6-STD (BLANK)	3109.00	8.79			
6-SAMPLE	547.00		1.55	13.56	39.28
6-SAMPLE	381.00		1.08	13.05	40.25

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: EBEN, WATER, MPP--BLANK CORRECTED

EQUILIBRATION TIME: 48 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 70753.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	641.00	1.81			
1-SAMPLE	268.00		0.76	13.60	5.74
1-SAMPLE	296.00		0.84	13.04	5.09
2-STD (BLANK)	6547.00	18.51			
2-SAMPLE	1364.00		3.86	13.62	79.82
2-SAMPLE	1501.00		4.24	13.52	77.14
3-STD (BLANK)	2197.00	6.21			
3-SAMPLE	637.00		1.80	13.43	23.69
3-SAMPLE	614.00		1.74	13.53	24.22
4-STD (BLANK)	10394.00	29.38			
4-SAMPLE	2462.00		6.96	13.72	123.05
4-SAMPLE	2641.00		7.47	13.63	119.48
5-STD (BLANK)	1974.00	5.58			
5-SAMPLE	700.00		1.98	13.46	19.39
5-SAMPLE	532.00		1.50	13.63	22.22
6-STD (BLANK)	24666.00	69.72			
6-SAMPLE	7313.00		20.67	13.84	271.55
6-SAMPLE	7046.00		19.92	13.27	264.38
7-STD (BLANK)	32161.00	90.91			
7-SAMPLE	7489.00		21.17	13.60	379.40
7-SAMPLE	8130.00		22.98	13.84	376.06
8-STD (BLANK)	40301.00	113.92			
8-SAMPLE	8228.00		23.26	13.65	495.01
8-SAMPLE	8118.00		22.95	13.59	494.53

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: EBEN, WATER, NATURAL--BLANK CORRECTED

EQUILIBRATION TIME: 24 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 70753.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	548.00	1.55			
1-SAMPLE	874.00		2.47	13.82	-5.09
1-SAMPLE	764.00		2.16	13.53	-3.30
2-STD (BLANK)	3723.00	10.52			
2-SAMPLE	2848.00		8.05	13.52	13.38
2-SAMPLE	3162.00		8.94	13.77	8.73
3-STD (BLANK)	41045.00	116.02			
3-SAMPLE	29128.00		82.34	13.50	181.91
3-SAMPLE	28862.00		81.59	13.53	186.38
4-STD (BLANK)	29945.00	84.65			
4-SAMPLE	25208.00		71.26	13.76	73.70
4-SAMPLE	25436.00		71.90	13.83	70.51

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 151927.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
5-STD (BLANK)	17172.00	22.61			
5-SAMPLE	25834.00		34.01	13.59	-61.99
5-SAMPLE	18329.00		24.13	13.45	-8.19
6-STD (BLANK)	44822.00	59.00			
6-SAMPLE	43691.00		57.52	13.84	8.24
6-SAMPLE	46151.00		60.75	13.80	-9.66

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: PCE, BENZENE, HDTMA--BLANK CORRECTED

EQUILIBRATION TIME: 4 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 41103.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	4072.00	19.81			
1-SAMPLE	4183.00		20.35	13.03	-2.82
1-SAMPLE	3896.00		18.96	12.94	4.43
2-STD (BLANK)	9766.00	47.52			
2-SAMPLE	9982.00		48.57	12.92	-5.43
2-SAMPLE	9967.00		48.50	13.34	-5.22
3-STD (BLANK)	19135.00	93.11			
3-SAMPLE	18891.00		91.92	12.73	6.06
3-SAMPLE	19294.00		93.88	13.32	-4.11
4-STD (BLANK)	45338.00	220.61			
4-SAMPLE	45409.00		220.95	13.27	-1.82
4-SAMPLE	46712.00		227.29	13.56	-36.25
5-STD (BLANK)	47082.00	229.10			
5-SAMPLE	49033.00		238.59	13.27	-50.38
5-SAMPLE	46514.00		226.33	13.07	14.46
6-STD (BLANK)	75798.00	368.82			
6-SAMPLE	75159.00		365.71	13.12	16.33
6-SAMPLE	75979.00		369.70	12.94	-4.55

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: PCE, BENZENE, MPP--BLANK CORRECTED

EQUILIBRATION TIME: 8 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 41103.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	4072.00	19.81			
1-SAMPLE	4126.00		20.08	13.76	-1.45
1-SAMPLE	3932.00		19.13	13.65	3.72
2-STD (BLANK)	9766.00	47.52			
2-SAMPLE	9698.00		47.19	13.22	1.75
2-SAMPLE	9877.00		48.06	13.73	-2.97
3-STD (BLANK)	18316.00	89.12			
3-SAMPLE	18288.00		88.99	13.51	0.74
3-SAMPLE	18613.00		90.57	13.22	-7.64
4-STD (BLANK)	43993.00	214.06			
4-SAMPLE	44367.00		215.88	13.55	-9.86
4-SAMPLE	45350.00		220.67	13.49	-35.63
5-STD (BLANK)	47082.00	229.10			
5-SAMPLE	48140.00		234.24	13.67	-28.14
5-SAMPLE	46234.00		224.97	13.39	22.11
6-STD (BLANK)	75798.00	368.82			
6-SAMPLE	74967.00		364.78	13.63	22.06
6-SAMPLE	75972.00		369.67	13.35	-4.51

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: PCE, BENZENE, NATURAL--BLANK CORRECTED

EQUILBRATION TIME: 24 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 41103.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	4207.00	20.47			
1-SAMPLE	4158.00		20.23	13.16	1.26
1-SAMPLE	4096.00		19.93	13.46	2.91
2-STD (BLANK)	9665.00	47.03			
2-SAMPLE	9642.00		46.92	13.14	0.59
2-SAMPLE	9966.00		48.49	13.04	-7.64
3-STD (BLANK)	19135.00	93.11			
3-SAMPLE	18592.00		90.47	13.73	14.52
3-SAMPLE	18979.00		92.35	13.31	4.05
4-STD (BLANK)	45338.00	220.61			
4-SAMPLE	43581.00		212.06	13.48	46.11
4-SAMPLE	45776.00		222.74	13.64	-11.61
5-STD (BLANK)	49073.00	238.78			
5-SAMPLE	48418.00		235.59	13.30	16.96
5-SAMPLE	48427.00		235.64	13.43	16.89
6-STD (BLANK)	75798.00	368.82			
6-SAMPLE	77969.00		379.38	13.68	-57.79
6-SAMPLE	74448.00		362.25	13.43	35.30

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: PCE, METHANOL, HDTMA--BLANK CORRECTED

EQUILIBRATION TIME: 4 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 42046.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	2597.00	12.35			
1-SAMPLE	3769.00		17.93	12.82	-28.59
1-SAMPLE	2803.00		13.33	13.10	-5.13
2-STD (BLANK)	6631.00	31.54			
2-SAMPLE	5852.00		27.84	12.95	19.19
2-SAMPLE	6076.00		28.90	13.32	14.07
3-STD (BLANK)	10477.00	49.84			
3-SAMPLE	9790.00		46.57	13.01	17.01
3-SAMPLE	9865.00		46.92	13.51	15.73
4-STD (BLANK)	19935.00	94.82			
4-SAMPLE	17228.00		81.95	13.32	68.61
4-SAMPLE	17604.00		83.74	13.43	59.56
5-STD (BLANK)	26402.00	125.59			
5-SAMPLE	25178.00		119.76	12.91	30.07
5-SAMPLE	25936.00		123.37	13.41	11.89

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: PCE, METHANOL, MPP--BLANK CORRECTED

EQUILIBRATION TIME: 8 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 42046.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	2597.00	12.35			
1-SAMPLE	3339.00		15.88	13.60	-19.20
1-SAMPLE	4162.00		19.80	13.35	-39.75
2-STD (BLANK)	6631.00	31.54			
2-SAMPLE	7073.00		33.64	12.86	-10.82
2-SAMPLE	7528.00		35.81	13.20	-22.53
3-STD (BLANK)	10477.00	49.84			
3-SAMPLE	12594.00		59.91	13.31	-53.61
3-SAMPLE	12201.00		58.04	13.46	-44.15
4-STD (BLANK)	19935.00	94.82			
4-SAMPLE	21596.00		102.73	13.41	-42.38
4-SAMPLE	22604.00		107.52	13.39	-68.00
5-STD (BLANK)	26402.00	125.59			
5-SAMPLE	22136.00		105.29	13.58	110.23
5-SAMPLE	23171.00		110.22	13.62	83.73

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: PCE, METHANOL, NATURAL--BLANK CORRECTED

EQUILIBRATION TIME: 24 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 42046.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	3472.00	16.52			
1-SAMPLE	4074.00		19.38	13.44	-15.39
1-SAMPLE	3726.00		17.72	12.72	-6.15
2-STD (BLANK)	8067.00	38.37			
2-SAMPLE	7110.00		33.82	13.03	23.73
2-SAMPLE	6780.00		32.25	13.17	32.25
3-STD (BLANK)	14931.00	71.02			
3-SAMPLE	14839.00		70.58	13.48	2.36
3-SAMPLE	15757.00		74.95	13.38	-21.03
4-STD (BLANK)	21828.00	103.83			
4-SAMPLE	20674.00		98.34	12.98	28.50
4-SAMPLE	18639.00		88.66	13.27	80.52

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 30441.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
5-STD (BLANK)	7616.00	50.04			
5-SAMPLE	7067.00		46.43	13.55	19.55
5-SAMPLE	7587.00		49.85	13.55	1.03
6-STD (BLANK)	26272.00	172.61			
6-SAMPLE	26484.00		174.00	13.49	-7.52
6-SAMPLE	25938.00		170.41	13.69	12.02

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: PCE, WATER, HDTMA--BLANK CORRECTED

EQUILIBRATION TIME: 4 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 26277.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	1582.00	12.04			
1-SAMPLE	102.00		0.78	12.99	58.53
1-SAMPLE	194.00		1.48	13.23	55.91
2-STD (BLANK)	3692.00	28.10			
2-SAMPLE	370.00		2.82	13.11	132.59
2-SAMPLE	252.00		1.92	13.33	139.61
3-STD (BLANK)	6595.00	50.20			
3-SAMPLE	736.00		5.60	13.32	237.60
3-SAMPLE	439.00		3.34	13.30	249.27
4-STD (BLANK)	9501.00	72.31			
4-SAMPLE	928.00		7.06	13.30	347.14
4-SAMPLE	923.00		7.03	12.83	335.06
5-STD (BLANK)	18103.00	134.95			
5-SAMPLE	1584.00		12.06	13.65	670.98
5-SAMPLE	1251.00		9.52	13.45	674.79
6-STD (BLANK)	25017.00	190.41			
6-SAMPLE	2469.00		18.79	13.09	898.59
6-SAMPLE	2402.00		18.28	13.56	933.62

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: PCE, WATER, MPP--BLANK CORRECTED

EQUILIBRATION TIME: 8 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 26277.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	1582.00	12.04			
1-SAMPLE	459.00		3.49	13.79	47.15
1-SAMPLE	299.00		2.28	13.73	53.63
2-STD (BLANK)	3692.00	28.10			
2-SAMPLE	795.00		6.05	13.26	116.95
2-SAMPLE	685.00		5.21	13.45	123.13
3-STD (BLANK)	6595.00	50.20			
3-SAMPLE	1415.00		10.77	13.60	214.48
3-SAMPLE	1287.00		9.80	13.22	213.64
4-STD (BLANK)	9501.00	72.31			
4-SAMPLE	2207.00		16.80	13.84	307.34
4-SAMPLE	2304.00		17.54	13.76	301.50
5-STD (BLANK)	18103.00	134.95			
5-SAMPLE	3068.00		23.35	13.37	596.81
5-SAMPLE	3004.00		22.86	13.86	621.39
6-STD (BLANK)	25017.00	190.41			
6-SAMPLE	4696.00		35.74	13.25	819.74
6-SAMPLE	4990.00		37.98	13.52	824.34

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: PCE, WATER, NATURAL--BLANK CORRECTED

EQUILIBRATION TIME: 24 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 26277.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	1544.00	11.75			
1-SAMPLE	1725.00		13.13	13.41	-7.39
1-SAMPLE	1582.00		12.04	13.55	-1.57
2-STD (BLANK)	3425.00	26.07			
2-SAMPLE	2734.00		20.81	13.58	28.57
2-SAMPLE	3151.00		23.98	13.25	11.05
3-STD (BLANK)	7473.00	56.88			
3-SAMPLE	5128.00		39.03	13.79	98.47
3-SAMPLE	6272.00		47.74	13.35	48.83
4-STD (BLANK)	9046.00	68.85			
4-SAMPLE	8552.00		65.09	13.50	20.30
4-SAMPLE	10406.00		79.20	13.75	-56.93
5-STD (BLANK)	23194.00	176.53			
5-SAMPLE	19890.00		151.39	13.73	138.11
5-SAMPLE	22219.00		169.11	13.62	40.43

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: TCA, BENZENE, HDTMA--BLANK CORRECTED

EQUILIBRATION TIME: 4 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 73887.76

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	2869.00	7.77			
1-SAMPLE	2492.00		6.75	13.34	5.45
1-SAMPLE	2571.00		6.96	13.52	4.36
2-STD (BLANK)	8490.00	22.98			
2-SAMPLE	9020.00		24.42	13.40	-7.69
2-SAMPLE	8572.00		23.20	13.58	-1.21
3-STD (BLANK)	20106.00	54.42			
3-SAMPLE	20034.00		54.23	13.28	1.04
3-SAMPLE	19513.00		52.82	13.40	8.60
4-STD (BLANK)	39237.00	106.21			
4-SAMPLE	40563.00		109.80	13.50	-19.38
4-SAMPLE	39900.00		108.00	13.32	-9.56
5-STD (BLANK)	52623.00	142.44			
5-SAMPLE	55220.00		149.47	13.65	-38.38
5-SAMPLE	54826.00		148.40	13.62	-32.49
6-STD (BLANK)	89227.00	241.52			
6-SAMPLE	88290.00		238.98	13.42	13.62
6-SAMPLE	87307.00		236.32	13.43	27.93

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: TCA, BENZENE, MPP--BLANK CORRECTED

EQUILIBRATION TIME: 8 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 73887.76

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	2869.00	7.77			
1-SAMPLE	2465.00		6.67	13.31	5.82
1-SAMPLE	2586.00		7.00	13.56	4.15
2-STD (BLANK)	8490.00	22.98			
2-SAMPLE	8853.00		23.96	13.47	-5.29
2-SAMPLE	10003.00		27.08	13.56	-22.21
3-STD (BLANK)	20106.00	54.42			
3-SAMPLE	19992.00		54.11	13.19	1.63
3-SAMPLE	20850.00		56.44	13.63	-10.98
4-STD (BLANK)	39237.00	106.21			
4-SAMPLE	40875.00		110.64	13.57	-24.07
4-SAMPLE	39727.00		107.53	13.79	-7.32
5-STD (BLANK)	52623.00	142.44			
5-SAMPLE	54529.00		147.60	13.38	-27.61
5-SAMPLE	53053.00		143.60	13.26	-6.17
6-STD (BLANK)	86821.00	235.01			
6-SAMPLE	86796.00		234.94	13.44	0.36
6-SAMPLE	85990.00		232.76	13.47	12.12

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: TCA, BENZENE, NATURAL--BLANK CORRECTED

EQUILIBRATION TIME: 24 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 73887.76

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	3191.00	8.64			
1-SAMPLE	2683.00		7.26	13.40	7.37
1-SAMPLE	2490.00		6.74	13.56	10.29
2-STD (BLANK)	8381.00	22.69			
2-SAMPLE	8049.00		21.79	13.49	4.85
2-SAMPLE	8523.00		23.07	13.09	-2.01
3-STD (BLANK)	18618.00	50.40			
3-SAMPLE	17601.00		47.64	13.57	14.94
3-SAMPLE	18169.00		49.18	13.51	6.57
4-STD (BLANK)	39237.00	106.21			
4-SAMPLE	37979.00		102.80	13.59	18.51
4-SAMPLE	37979.00		102.80	13.16	17.92
5-STD (BLANK)	59653.00	161.47			
5-SAMPLE	59755.00		161.75	13.32	-1.47
5-SAMPLE	58762.00		159.06	13.47	12.99
6-STD (BLANK)	98303.00	266.09			
6-SAMPLE	99026.00		268.04	13.64	-10.68
6-SAMPLE	99756.00		270.02	13.89	-21.85

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: TCA, METHANOL, HDTMA--BLANK CORRECTED

EQUILIBRATION TIME: 4 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 66388.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	1917.00	5.78			
1-SAMPLE	1764.00		5.31	13.20	2.43
1-SAMPLE	1888.00		5.69	13.00	0.45
2-STD (BLANK)	8951.00	26.97			
2-SAMPLE	8430.00		25.40	12.62	7.92
2-SAMPLE	7691.00		23.17	13.14	19.95
3-STD (BLANK)	13843.00	41.70			
3-SAMPLE	14777.00		44.52	12.52	-14.09
3-SAMPLE	13509.00		40.70	12.98	5.22
4-STD (BLANK)	29243.00	88.10			
4-SAMPLE	29106.00		87.68	13.15	2.17
4-SAMPLE	28931.00		87.16	13.22	4.97
5-STD (BLANK)	80377.00	241.69			
5-SAMPLE	78435.00		236.29	13.24	28.60
5-SAMPLE	80690.00		243.09	13.31	-7.42

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: TCA, METHANOL, MPP--BLANK CORRECTED

EQUILIBRATION TIME: 8 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 65439.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	2002.00	6.12			
1-SAMPLE	2126.00		6.50	13.55	-2.05
1-SAMPLE	1893.00		5.79	12.82	1.71
2-STD (BLANK)	7647.00	23.37			
2-SAMPLE	8139.00		24.88	13.02	-7.83
2-SAMPLE	7991.00		24.42	13.57	-5.71
3-STD (BLANK)	13806.00	42.20			
3-SAMPLE	15115.00		46.20	13.32	-21.32
3-SAMPLE	13653.00		41.73	13.29	2.49
4-STD (BLANK)	30270.00	92.51			
4-SAMPLE	27005.00		82.53	13.39	53.45
4-SAMPLE	29450.00		90.01	13.32	13.35

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 114487.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
5-STD (BLANK)	96480.00	168.54			
5-SAMPLE	89354.00		156.09	13.64	67.92
5-SAMPLE	95458.00		166.76	13.49	9.64

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: TCA, METHANOL, NATURAL--BLANK CORRECTED

EQUILIBRATION TIME: 24 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 66388.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	1917.00	5.78			
1-SAMPLE	1898.00		5.72	13.11	0.30
1-SAMPLE	1917.00		5.78	13.20	0.00
2-STD (BLANK)	8951.00	26.97			
2-SAMPLE	7835.00		23.60	13.34	17.94
2-SAMPLE	7640.00		23.02	13.45	21.25
3-STD (BLANK)	13843.00	41.70			
3-SAMPLE	12947.00		39.00	12.96	13.99
3-SAMPLE	12873.00		38.78	13.15	15.37
4-STD (BLANK)	27985.00	84.31			
4-SAMPLE	25832.00		77.82	13.35	34.64
4-SAMPLE	28881.00		87.01	12.86	-13.89
5-STD (BLANK)	80377.00	241.69			
5-SAMPLE	76453.00		230.32	13.07	59.45
5-SAMPLE	78258.00		235.76	13.32	31.61

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: TCA, WATER, HDTMA--BLANK CORRECTED

EQUILIBRATION TIME: 4 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 58837.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	676.00	2.30			
1-SAMPLE	469.00		1.59	12.72	3.58
1-SAMPLE	183.00		0.62	12.97	8.69
2-STD (BLANK)	3247.00	11.04			
2-SAMPLE	811.00		2.76	12.94	42.86
2-SAMPLE	909.00		3.09	13.51	42.95
3-STD (BLANK)	6859.00	23.32			
3-SAMPLE	1769.00		6.01	13.02	90.11
3-SAMPLE	1482.00		5.04	13.13	95.99
4-STD (BLANK)	21894.00	74.42			
4-SAMPLE	5271.00		17.92	13.47	304.45
4-SAMPLE	4123.00		14.01	13.27	320.64
5-STD (BLANK)	37087.00	125.79			
5-SAMPLE	9982.00		33.93	13.01	478.02
5-SAMPLE	6497.00		22.08	12.87	533.86

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: TCA, WATER, MPP--BLANK CORRECTED

EQUILIBRATION TIME: 8 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 63555.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	370.00	1.16			
1-SAMPLE	284.00		0.89	13.61	1.47
1-SAMPLE	300.00		0.94	13.78	1.21
2-STD (BLANK)	6528.00	20.54			
2-SAMPLE	5338.00		16.80	13.51	20.24
2-SAMPLE	5171.00		16.27	13.36	22.82
3-STD (BLANK)	12839.00	40.40			
3-SAMPLE	9058.00		28.50	13.39	63.73
3-SAMPLE	10465.00		32.93	13.24	39.56
4-STD (BLANK)	23131.00	72.79			
4-SAMPLE	20071.00		63.16	13.38	51.54
4-SAMPLE	18427.00		57.99	13.60	80.53
5-STD (BLANK)	36984.00	116.38			
5-SAMPLE	29881.00		94.03	13.52	120.88
5-SAMPLE	27969.00		88.02	13.34	151.38
6-STD (BLANK)	58203.00	183.16			
6-SAMPLE	46236.00		145.50	13.42	202.15
6-SAMPLE	49596.00		156.07	13.48	146.04

SPREADSHEET FOR ISOTHERM CALCULATION FROM GC DATA

MASS OF ZEOLITE: 2.50 g

SOLUTE, SOLVENT, ZEOLITE: TCA, WATER, NATURAL--BLANK CORRECTED

EQUILIBRATION TIME: 24 HOURS

FACTORY STANDARD CONCENTRATION (mg/l): 200.00
INTEGRATOR AREA OF FACTORY STANDARD: 58837.00

SAMPLE NUMBER	INTEGRATOR AREA	SOL'N INIT. CONC. (mg/l)	EQUIL. SOL'N CONC. (mg/l)	SOL'N VOL. (ml)	SOLUTE MASS SORBED (mg/kg)
1-STD (BLANK)	676.00	2.30			
1-SAMPLE	1185.00		4.03	13.67	-9.46
1-SAMPLE	884.00		3.00	13.81	-3.91
2-STD (BLANK)	3247.00	11.04			
2-SAMPLE	3375.00		11.47	13.53	-2.35
2-SAMPLE	3401.00		11.56	13.28	-2.78
3-STD (BLANK)	6859.00	23.32			
3-SAMPLE	6701.00		22.78	13.31	2.86
3-SAMPLE	7670.00		26.07	13.28	-14.64
4-STD (BLANK)	21894.00	74.42			
4-SAMPLE	19745.00		67.12	13.44	39.27
4-SAMPLE	21500.00		73.08	13.23	7.09
5-STD (BLANK)	20057.00	68.18			
5-SAMPLE	19980.00		67.92	13.31	1.39
5-SAMPLE	17753.00		60.35	13.62	42.67
6-STD (BLANK)	31194.00	106.04			
6-SAMPLE	28799.00		97.89	13.41	43.67
6-SAMPLE	29170.00		99.16	13.67	37.62

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO HDTMA ZEOLITE FROM AQUEOUS SOLUTION

Stock Solution Preparation:   50140.00 mg
                                 99.00% purity                           EQUILIBRIUM
                         in       1000 ml                              --------------------
Stock Solution :   49638.60 mg/l                                 Liq       Liq      Sorbed
Solution Volume = 5.00 ml                                        Conc.     Conc      Conc
C-14 solution:       14.00 mg/l                                  (cpm/ml)  (mg/l)   (mg/kg)

Equilibration Time:  8 Hours

************************************************************
Tube Set:    1    (100 mg/l)                   Tube 1        4236.08      6.65    185.38
                                                  2.50 g soil
Concentration relative to stock:         0.002

C-14 spike:
  175.00 ul, added to          40.00 ml
                                              Tube 1D        3975.60      6.24    186.20
Actual sol'n concentration:     99.34    mg/l     2.50 g soil
Average CPM of solution:     63300.45

************************************************************
Tube Set:    2    (1000 mg/l)                  Tube 2        4888.40     69.61   1846.45
                                                  2.50 g soil
Concentration relative to stock:         0.020

C-14 spike:
  175.00 ul, added to          40.00 ml
                                              Tube 2D        4148.29     59.07   1867.52
Actual sol'n concentration:    992.83    mg/l     2.50 g soil
Average CPM of solution:     69721.80

************************************************************
Tube Set:    3    (5000 mg/l)                  Tube 3        4011.22    305.88   9316.09
                                                  2.50 g soil
Concentration relative to stock:         0.100

C-14 spike:
  175.00 ul, added to          40.00 ml
                                               Tube 3D       4144.62    316.05   9295.74
Actual sol'n concentration:   4963.92    mg/l     2.50 g soil
Average CPM of solution:     65095.80

************************************************************
Tube Set:    4    (10000 mg/l)                 Tube 4        4690.27    668.52  18518.53
                                                  2.50 g soil
Concentration relative to stock:         0.200

C-14 spike:
  175.00 ul, added to          40.00 ml
                                               Tube 4D       4827.74    688.11  18479.34
Actual sol'n concentration:   9927.78    mg/l     2.50 g soil
Average CPM of solution:     69652.55

************************************************************
Tube Set:    5    (25000 mg/l)                 Tube 5        7093.97   2512.90  44612.92
                                                  2.50 g soil
Concentration relative to stock:         0.500

C-14 spike:
  175.00 ul, added to          40.00 ml
                                               Tube 5D       7964.41   2821.24  43996.25
Actual sol'n concentration:  24819.36    mg/l     2.50 g soil
Average CPM of solution:     70065.55
************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO HDTMA ZEOLITE FROM AQUEOUS SOLUTION

Stock Solution Preparation:   50140.00 mg
                                 99.00% purity                        EQUILIBRIUM
                        in        1000 ml                        --------------------
Stock Solution :   49638.60 mg/l                           Liq       Liq      Sorbed
Solution Volume = 5.00 ml                                 Conc.     Conc      Conc
C-14 solution:         14.00 mg/l                        (cpm/ml)  (mg/l)    (mg/kg)

Equilibration Time:  8 Hours

*************************************************************
Tube Set:    6    (50000 mg/l)              Tube 6        19540.90  13367.57  72542.19
                                               2.50 g soil
Concentration relative to stock:         1.000

C-14 spike:
  175.00 ul, added to            40.00 ml
                                            Tube 6D       19560.90  13381.25  72514.82
Actual sol'n concentration:   49638.66    mg/l     2.50 g soil
Average CPM of solution:      72562.50
*************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO HDTMA ZEOLITE FROM BENZENE SOLUTION

Stock Solution Preparation:   50800.00 mg
                                 99.00% purity                           EQUILIBRIUM
                          in      1000 ml                           --------------------
Stock Solution :   50292.00 mg/l                               Liq       Liq      Sorbed
Solution Volume = 5.00 ml                                     Conc.      Conc      Conc
C-14 solution:        14.00 mg/l                            (cpm/ml)   (mg/l)    (mg/kg)

Equilibration Time:  24 Hours

************************************************************
Tube Set:    1    (100 mg/l)                   Tube 1       214.30      2.35     196.49
                                                  2.50 g soil
Concentration relative to stock:         0.002

C-14 spike:
   25.00 ul, added to            40.00 ml
                                              Tube 1D       299.60      3.28     194.62
Actual sol'n concentration:     100.59   mg/l     2.50 g soil
Average CPM of solution:       9175.89

************************************************************
Tube Set:    2    (1000 mg/l)                  Tube 2       287.90     28.92    1953.86
                                                  2.50 g soil
Concentration relative to stock:         0.020

C-14 spike:
   25.00 ul, added to            40.00 ml
                                              Tube 2D       281.60     28.29    1955.12
Actual sol'n concentration:    1005.85   mg/l     2.50 g soil
Average CPM of solution:      10012.85

************************************************************
Tube Set:    3    (5000 mg/l)                  Tube 3       562.40    292.75    9472.91
                                                  2.50 g soil
Concentration relative to stock:         0.100

C-14 spike:
   25.00 ul, added to            40.00 ml
                                               Tube 3D      779.30    405.66    9247.10
Actual sol'n concentration:    5029.21   mg/l     2.50 g soil
Average CPM of solution:       9661.53

************************************************************
Tube Set:    4    (10000 mg/l)                 Tube 4      1564.10   1687.53   16741.75
                                                  2.50 g soil
Concentration relative to stock:         0.200

C-14 spike:
   25.00 ul, added to            40.00 ml
                                               Tube 4D     1430.20   1543.07   17030.68
Actual sol'n concentration:   10058.41   mg/l     2.50 g soil
Average CPM of solution:       9322.69

************************************************************
Tube Set:    5    (25000 mg/l)                 Tube 5      3312.70   8682.35   32927.31
                                                  2.50 g soil
Concentration relative to stock:         0.500

C-14 spike:
   25.00 ul, added to            40.00 ml
                                               Tube 5D     3473.00   9102.49   32087.04
Actual sol'n concentration:   25146.01   mg/l     2.50 g soil
Average CPM of solution:       9594.31
************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO HDTMA ZEOLITE FROM BENZENE SOLUTION

Stock Solution Preparation:   50800.00 mg
                                 99.00% purity                              EQUILIBRIUM
                          in      1000 ml                          --------------------
Stock Solution :   50292.00 mg/l                            Liq      Liq      Sorbed
Solution Volume = 5.00 ml                                  Conc.     Conc      Conc
C-14 solution:         14.00 mg/l                         (cpm/ml)  (mg/l)   (mg/kg)

Equilibration Time:  24 Hours

************************************************************
Tube Set:    6    (50000 mg/l)              Tube 6        5464.89  28947.38  42689.26
                                              2.50 g soil
Concentration relative to stock:        1.000

C-14 spike:
   25.00 ul, added to            40.00 ml
                                            Tube 6D       5410.41  28658.80  43266.42
Actual sol'n concentration:   50292.01   mg/l    2.50 g soil
Average CPM of solution:       9494.48
************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO HDTMA ZEOLITE FROM METHANOL SOLUTION

Stock Solution Preparation:   50280.00 mg
                                 99.00% purity                          EQUILIBRIUM
                        in       1000 ml                          --------------------
Stock Solution :   49777.20 mg/l                           Liq      Liq      Sorbed
Solution Volume = 5.00 ml                                  Conc.    Conc     Conc
C-14 solution:          14.00 mg/l                        (cpm/ml)  (mg/l)   (mg/kg)

Equilibration Time:  8 Hours

*************************************************************
Tube Set:    1   (100 mg/l)                Tube 1     18322.80     70.36     58.45
                                              2.50 g soil
Concentration relative to stock:         0.002

C-14 spike:
  100.00 ul, added to          40.00 ml
                                           Tube 1D    21794.00     83.69     31.79
Actual sol'n concentration:     99.59   mg/l  2.50 g soil
Average CPM of solution:     25933.60

*************************************************************
Tube Set:    2   (1000 mg/l)               Tube 2     31291.40    769.47    452.21
                                              2.50 g soil
Concentration relative to stock:         0.020

C-14 spike:
  100.00 ul, added to          40.00 ml
                                           Tube 2D    34498.20    848.33    294.50
Actual sol'n concentration:    995.58   mg/l  2.50 g soil
Average CPM of solution:     40486.25

*************************************************************
Tube Set:    3   (5000 mg/l)               Tube 3     32956.50   3882.84   2189.83
                                              2.50 g soil
Concentration relative to stock:         0.100

C-14 spike:
  100.00 ul, added to          40.00 ml
                                           Tube 3D    31928.50   3761.72   2432.06
Actual sol'n concentration:   4977.76   mg/l  2.50 g soil
Average CPM of solution:     42249.85

*************************************************************
Tube Set:    4   (10000 mg/l)              Tube 4     32316.10   8036.03   3838.89
                                              2.50 g soil
Concentration relative to stock:         0.200

C-14 spike:
  100.00 ul, added to          40.00 ml
                                           Tube 4D    32105.60   7983.69   3943.58
Actual sol'n concentration:   9955.48   mg/l  2.50 g soil
Average CPM of solution:     40034.95

*************************************************************
Tube Set:    5   (25000 mg/l)              Tube 5     30515.90  19891.08   9995.11
                                              2.50 g soil
Concentration relative to stock:         0.500

C-14 spike:
  100.00 ul, added to          40.00 ml
                                           Tube 5D    29688.80  19351.95  11073.36
Actual sol'n concentration:  24888.64   mg/l  2.50 g soil
Average CPM of solution:     38182.90
*************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO HDTMA ZEOLITE FROM METHANOL SOLUTION

Stock Solution Preparation:   50280.00 mg
                                99.00% purity                              EQUILIBRIUM
                          in      1000 ml                              --------------------
Stock Solution :   49777.20 mg/l                                  Liq      Liq      Sorbed
Solution Volume = 5.00 ml                                        Conc.    Conc      Conc
C-14 solution:        14.00 mg/l                               (cpm/ml)  (mg/l)   (mg/kg)

Equilibration Time:  8 Hours

*************************************************************
Tube Set:    6    (50000 mg/l)                   Tube 6        31651.10  38954.05  21646.37
                                                    2.50 g soil
Concentration relative to stock:           1.000

C-14 spike:
  100.00 ul, added to            40.00 ml
                                                 Tube 6D       34270.00  42177.21  15200.04
Actual sol'n concentration:   49777.24   mg/l       2.50 g soil
Average CPM of solution:      40445.20
*************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FROM C14 DATA

PHENOL TO MPP ZEOLITE FROM AQUEOUS SOLUTION

Stock Solution Preparation:   50140.00 mg
                                99.00% purity                           EQUILIBRIUM
                          in    1000 ml                       -------------------
Stock Solution :   49638.60 mg/l                              Liq       Liq     Sorbed
Solution Volume = 5.00 ml                                    Conc.     Conc      Conc
C-14 solution:         14.00 mg/l                          (cpm/ml)   (mg/l)   (mg/kg)

Equilibration Time:  8 Hours

*************************************************************
Tube Set:     1    (100 mg/l)                Tube 1            6258.59      9.82     179.03
                                                 2.50  g soil
Concentration relative to stock:         0.002

C-14 spike:
  175.00 ul, added to          40.00 ml
                                             Tube 1D           6324.01      9.92     178.83
Actual sol'n concentration:      99.34   mg/l    2.50  g soil
Average CPM of solution:      63300.45

*************************************************************
Tube Set:     2    (1000 mg/l)               Tube 2            7742.17    110.25    1765.17
                                                 2.50  g soil
Concentration relative to stock:         0.020

C-14 spike:
  175.00 ul, added to          40.00 ml
                                             Tube 2D           7937.90    113.04    1759.60
Actual sol'n concentration:     992.83   mg/l    2.50  g soil
Average CPM of solution:      69721.80

*************************************************************
Tube Set:     3    (5000 mg/l)               Tube 3           19940.80   1520.60    6886.65
                                                 2.50  g soil
Concentration relative to stock:         0.100

C-14 spike:
  175.00 ul, added to          40.00 ml
                                             Tube 3D          20871.30   1591.55    6744.73
Actual sol'n concentration:    4963.92   mg/l    2.50  g soil
Average CPM of solution:      65095.80

*************************************************************
Tube Set:     4    (10000 mg/l)              Tube 4           35151.70   5010.27    9835.01
                                                 2.50  g soil
Concentration relative to stock:         0.200

C-14 spike:
  175.00 ul, added to          40.00 ml
                                             Tube 4D          34876.50   4971.05    9913.46
Actual sol'n concentration:    9927.78   mg/l    2.50  g soil
Average CPM of solution:      69652.55

*************************************************************
Tube Set:     5    (25000 mg/l)              Tube 5           44718.80  15840.77   17957.19
                                                 2.50  g soil
Concentration relative to stock:         0.500

C-14 spike:
  175.00 ul, added to          40.00 ml
                                             Tube 5D          45651.10  16171.02   17296.69
Actual sol'n concentration:   24819.36   mg/l    2.50  g soil
Average CPM of solution:      70065.55
*************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FROM C14 DATA

PHENOL TO MPP ZEOLITE FROM AQUEOUS SOLUTION

Stock Solution Preparation:   50140.00 mg
                                 99.00% purity                            EQUILIBRIUM
                       in        1000 ml                              -------------------
Stock Solution :   49638.60 mg/l                                  Liq       Liq      Sorbed
Solution Volume = 5.00 ml                                        Conc.     Conc      Conc
C-14 solution:        14.00 mg/l                               (cpm/ml)   (mg/l)   (mg/kg)

Equilibration Time:  8 Hours

***************************************************************
Tube Set:    6   (50000 mg/l)                  Tube 6           49822.20  34082.44  31112.44
                                                  2.50  g soil
Concentration relative to stock:         1.000

C-14 spike:
  175.00 ul, added to            40.00 ml
                                               Tube 6D          50068.70  34251.07  30775.18
Actual sol'n concentration:   49638.66   mg/l     2.50  g soil
Average CPM of solution:      72562.50
***************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO MPP ZEOLITE FROM BENZENE SOLUTION

Stock Solution Preparation:   50800.00 mg
                                 99.00% purity                              EQUILIBRIUM
                            in     1000 ml                           --------------------
Stock Solution :    50292.00 mg/l                           Liq        Liq       Sorbed
Solution Volume = 5.00 ml                                   Conc.      Conc       Conc
C-14 solution:          14.00 mg/l                          (cpm/ml)   (mg/l)     (mg/kg)

Equilibration Time:  24 Hours

*****************************************************************
Tube Set:    1    (100 mg/l)                 Tube 1         1947.80     21.35     158.48
                                                2.50 g soil
Concentration relative to stock:        0.002

C-14 spike:
   25.00 ul, added to            40.00 ml
                                             Tube 1D        1986.60     21.78     157.63
Actual sol'n concentration:      100.59   mg/l  2.50 g soil
Average CPM of solution:        9175.89

*****************************************************************
Tube Set:    2    (1000 mg/l)                Tube 2         2607.70    261.96    1487.78
                                                2.50 g soil
Concentration relative to stock:        0.020

C-14 spike:
   25.00 ul, added to            40.00 ml
                                             Tube 2D        2602.80    261.47    1488.76
Actual sol'n concentration:     1005.85   mg/l  2.50 g soil
Average CPM of solution:       10012.85

*****************************************************************
Tube Set:    3    (5000 mg/l)                Tube 3         3623.90   1886.38    6285.65
                                                2.50 g soil
Concentration relative to stock:        0.100

C-14 spike:
   25.00 ul, added to            40.00 ml
                                             Tube 3D        3569.90   1858.27    6341.87
Actual sol'n concentration:     5029.21   mg/l  2.50 g soil
Average CPM of solution:        9661.53

*****************************************************************
Tube Set:    4    (10000 mg/l)               Tube 4         4742.89   5117.18    9882.45
                                                2.50 g soil
Concentration relative to stock:        0.200

C-14 spike:
   25.00 ul, added to            40.00 ml
                                             Tube 4D        4460.53   4812.54   10491.73
Actual sol'n concentration:    10058.41   mg/l  2.50 g soil
Average CPM of solution:        9322.69

*****************************************************************
Tube Set:    5    (25000 mg/l)               Tube 5         6305.20  16525.48   17241.05
                                                2.50 g soil
Concentration relative to stock:        0.500

C-14 spike:
   25.00 ul, added to            40.00 ml
                                             Tube 5D        6263.22  16415.46   17461.10
Actual sol'n concentration:    25146.01   mg/l  2.50 g soil
Average CPM of solution:        9594.31
*****************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO MPP ZEOLITE FROM BENZENE SOLUTION

Stock Solution Preparation:   50800.00 mg
                                 99.00% purity                              EQUILIBRIUM
                         in        1000 ml                         -------------------
Stock Solution :   50292.00 mg/l                             Liq      Liq       Sorbed
Solution Volume = 5.00 ml                                   Conc.     Conc       Conc
C-14 solution:          14.00 mg/l                        (cpm/ml)  (mg/l)    (mg/kg)

Equilibration Time:  24 Hours

*************************************************************
Tube Set:    6    (50000 mg/l)                 Tube 6       7221.30  38251.03  24081.95
                                                  2.50 g soil
Concentration relative to stock:          1.000

C-14 spike:
   25.00 ul, added to             40.00 ml
                                               Tube 6D      7190.31  38086.88  24410.25
Actual sol'n concentration:   50292.01    mg/l    2.50 g soil
Average CPM of solution:      9494.48
*************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO MPP ZEOLITE FROM METHANOL SOLUTION

Stock Solution Preparation:   50280.00 mg
                                99.00% purity                          EQUILIBRIUM
                        in      1000 ml                           ------------------
Stock Solution :   49777.20 mg/l                            Liq      Liq      Sorbed
Solution Volume = 5.00 ml                                  Conc.     Conc      Conc
C-14 solution:         14.00 mg/l                        (cpm/ml)   (mg/l)   (mg/kg)

Equilibration Time:  8 Hours

*************************************************************
Tube Set:    1    (100 mg/l)                  Tube 1       16091.90    61.80     75.59
                                                2.50 g soil
Concentration relative to stock:          0.002

C-14 spike:
  100.00 ul, added to            40.00 ml
                                             Tube 1D       18764.00    72.06     55.06
Actual sol'n concentration:      99.59   mg/l    2.50 g soil
Average CPM of solution:       25933.60

*************************************************************
Tube Set:    2    (1000 mg/l)                 Tube 2       26840.00   660.01    671.14
                                                2.50 g soil
Concentration relative to stock:          0.020

C-14 spike:
  100.00 ul, added to            40.00 ml
                                             Tube 2D       28692.80   705.57    580.01
Actual sol'n concentration:     995.58   mg/l    2.50 g soil
Average CPM of solution:       40486.25

*************************************************************
Tube Set:    3    (5000 mg/l)                 Tube 3       28851.00  3399.14   3157.23
                                                2.50 g soil
Concentration relative to stock:          0.100

C-14 spike:
  100.00 ul, added to            40.00 ml
                                             Tube 3D       33288.40  3921.94   2111.62
Actual sol'n concentration:    4977.76   mg/l    2.50 g soil
Average CPM of solution:       42249.85

*************************************************************
Tube Set:    4    (10000 mg/l)                Tube 4       31359.30  7798.10   4314.74
                                                2.50 g soil
Concentration relative to stock:          0.200

C-14 spike:
  100.00 ul, added to            40.00 ml
                                             Tube 4D       34675.80  8622.82   2665.32
Actual sol'n concentration:    9955.48   mg/l    2.50 g soil
Average CPM of solution:       40034.95

*************************************************************
Tube Set:    5    (25000 mg/l)                Tube 5       30181.90 19673.37  10430.53
                                                2.50 g soil
Concentration relative to stock:          0.500

C-14 spike:
  100.00 ul, added to            40.00 ml
                                             Tube 5D       31365.60 20444.94   8887.40
Actual sol'n concentration:   24888.64   mg/l    2.50 g soil
Average CPM of solution:       38182.90
*************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO MPP ZEOLITE FROM METHANOL SOLUTION

Stock Solution Preparation:   50280.00 mg
                                 99.00% purity                         EQUILIBRIUM
                         in       1000 ml                     --------------------
Stock Solution :   49777.20 mg/l                            Liq      Liq      Sorbed
Solution Volume = 5.00 ml                                   Conc.    Conc     Conc
C-14 solution:        14.00 mg/l                          (cpm/ml)  (mg/l)   (mg/kg)

Equilibration Time:  8 Hours

************************************************************
Tube Set:    6    (50000 mg/l)               Tube 6       29774.80  36644.82  26264.82
                                                2.50 g soil
Concentration relative to stock:         1.000

C-14 spike:
  100.00 ul, added to            40.00 ml
                                             Tube 6D      37081.40  45637.30   8279.88
Actual sol'n concentration:   49777.24    mg/l    2.50 g soil
Average CPM of solution:      40445.20
************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO NATURAL ZEOLITE FROM AQUEOUS SOLUTION

Stock Solution Preparation:   50140.00 mg
                                  99.00% purity                          EQUILIBRIUM
                        in        1000 ml                          -------------------
Stock Solution :   49638.60 mg/l                          Liq       Liq       Sorbed
Solution Volume = 5.00 ml                                Conc.      Conc      Conc
C-14 solution:         14.00 mg/l                       (cpm/ml)   (mg/l)    (mg/kg)

Equilibration Time:  8 Hours

**************************************************************
Tube Set:    1    (100 mg/l)                   Tube 1      56596.00     88.82     21.04
                                                 2.50 g soil
Concentration relative to stock:         0.002

C-14 spike:
  175.00 ul, added to           40.00 ml
                                               Tube 1D     59400.00     93.22     12.24
Actual sol'n concentration:     99.34   mg/l     2.50 g soil
Average CPM of solution:      63300.45

**************************************************************
Tube Set:    2    (1000 mg/l)                  Tube 2      65466.10    932.23    121.20
                                                 2.50 g soil
Concentration relative to stock:         0.020

C-14 spike:
  175.00 ul, added to           40.00 ml
                                               Tube 2D     67433.30    960.25     65.18
Actual sol'n concentration:    992.83   mg/l     2.50 g soil
Average CPM of solution:      69721.80

**************************************************************
Tube Set:    3    (5000 mg/l)                  Tube 3      62596.80   4773.36    381.13
                                                 2.50 g soil
Concentration relative to stock:         0.100

C-14 spike:
  175.00 ul, added to           40.00 ml
                                               Tube 3D     63379.60   4833.05    261.74
Actual sol'n concentration:   4963.92   mg/l     2.50 g soil
Average CPM of solution:      65095.80

**************************************************************
Tube Set:    4    (10000 mg/l)                 Tube 4      65729.50   9368.62   1118.33
                                                 2.50 g soil
Concentration relative to stock:         0.200

C-14 spike:
  175.00 ul, added to           40.00 ml
                                               Tube 4D     67251.60   9585.57    684.43
Actual sol'n concentration:   9927.78   mg/l     2.50 g soil
Average CPM of solution:      69652.55

**************************************************************
Tube Set:    5    (25000 mg/l)                 Tube 5      62671.80  22200.27   5238.18
                                                 2.50 g soil
Concentration relative to stock:         0.500

C-14 spike:
  175.00 ul, added to           40.00 ml
                                               Tube 5D     62220.00  22040.23   5558.27
Actual sol'n concentration:  24819.36   mg/l     2.50 g soil
Average CPM of solution:      70065.55
**************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO NATURAL ZEOLITE FROM AQUEOUS SOLUTION

Stock Solution Preparation:   50140.00 mg
                                 99.00% purity                     EQUILIBRIUM
                      in          1000 ml                      --------------------
Stock Solution :   49638.60 mg/l                          Liq       Liq      Sorbed
Solution Volume = 5.00 ml                                Conc.      Conc      Conc
C-14 solution:        14.00 mg/l                        (cpm/ml)   (mg/l)   (mg/kg)

Equilibration Time:  8 Hours

************************************************************
Tube Set:    6   (50000 mg/l)              Tube 6        62659.30  42864.07  13549.19
                                             2.50 g soil
Concentration relative to stock:        1.000

C-14 spike:
  175.00 ul, added to          40.00 ml
                                           Tube 6D       64344.40  44016.81  11243.70
Actual sol'n concentration:   49638.66   mg/l    2.50 g soil
Average CPM of solution:      72562.50
************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO NATURAL ZEOLITE FROM BENZENE SOLUTION

Stock Solution Preparation:   50800.00 mg
                                 99.00% purity                              EQUILIBRIUM
                        in        1000 ml                              -------------------
Stock Solution :   50292.00 mg/l                              Liq        Liq       Sorbed
Solution Volume = 5.00 ml                                     Conc.      Conc       Conc
C-14 solution:        14.00 mg/l                             (cpm/ml)   (mg/l)    (mg/kg)

Equilibration Time:  24 Hours

**************************************************************
Tube Set:    1    (100 mg/l)                  Tube 1         5143.44     56.39      88.41
                                                 2.50 g soil
Concentration relative to stock:          0.002

C-14 spike:
   25.00 ul, added to           40.00 ml
                                             Tube 1D         5538.73     60.72      79.75
Actual sol'n concentration:    100.59   mg/l     2.50 g soil
Average CPM of solution:      9175.89

**************************************************************
Tube Set:    2    (1000 mg/l)                 Tube 2         5515.56    554.07     903.56
                                                 2.50 g soil
Concentration relative to stock:          0.020

C-14 spike:
   25.00 ul, added to           40.00 ml
                                             Tube 2D         5732.09    575.82     860.05
Actual sol'n concentration:   1005.85   mg/l     2.50 g soil
Average CPM of solution:     10012.85

**************************************************************
Tube Set:    3    (5000 mg/l)                 Tube 3         5650.00   2941.05    4176.32
                                                 2.50 g soil
Concentration relative to stock:          0.100

C-14 spike:
   25.00 ul, added to           40.00 ml
                                             Tube 3D         6107.33   3179.11    3700.20
Actual sol'n concentration:   5029.21   mg/l     2.50 g soil
Average CPM of solution:      9661.53

**************************************************************
Tube Set:    4    (10000 mg/l)                Tube 4         6609.90   7131.53    5853.75
                                                 2.50 g soil
Concentration relative to stock:          0.200

C-14 spike:
   25.00 ul, added to           40.00 ml
                                             Tube 4D         6050.15   6527.61    7061.60
Actual sol'n concentration:  10058.41   mg/l     2.50 g soil
Average CPM of solution:      9322.69

**************************************************************
Tube Set:    5    (25000 mg/l)                Tube 5         7069.96  18529.87   13232.29
                                                 2.50 g soil
Concentration relative to stock:          0.500

C-14 spike:
   25.00 ul, added to           40.00 ml
                                             Tube 5D         7047.89  18472.02   13347.97
Actual sol'n concentration:  25146.01   mg/l     2.50 g soil
Average CPM of solution:      9594.31
**************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO NATURAL ZEOLITE FROM BENZENE SOLUTION

Stock Solution Preparation:   50800.00 mg
                                 99.00% purity                         EQUILIBRIUM
                       in         1000 ml                       --------------------
Stock Solution :   50292.00 mg/l                             Liq       Liq      Sorbed
Solution Volume = 5.00 ml                                   Conc.      Conc      Conc
C-14 solution:        14.00 mg/l                          (cpm/ml)   (mg/l)    (mg/kg)

Equilibration Time:  24 Hours

************************************************************
Tube Set:    6    (50000 mg/l)                 Tube 6       8351.98  44240.22  12103.58
                                                 2.50 g soil
Concentration relative to stock:          1.000

C-14 spike:
   25.00 ul, added to            40.00 ml
                                               Tube 6D      7551.89  40002.16  20579.70
Actual sol'n concentration:   50292.01   mg/l    2.50 g soil
Average CPM of solution:       9494.48
************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO NATURAL ZEOLITE FROM METHANOL SOLUTION

Stock Solution Preparation:   50280.00 mg
                                 99.00% purity                              EQUILIBRIUM
                        in        1000 ml                          --------------------
Stock Solution :   49777.20 mg/l                            Liq       Liq      Sorbed
Solution Volume = 5.00 ml                                  Conc.      Conc      Conc
C-14 solution:        14.00 mg/l                         (cpm/ml)   (mg/l)    (mg/kg)

Equilibration Time:  8 Hours

************************************************************
Tube Set:    1    (100 mg/l)                 Tube 1      22850.50     87.75      23.68
                                               2.50 g soil
Concentration relative to stock:        0.002

C-14 spike:
  100.00 ul, added to           40.00 ml
                                             Tube 1D     25578.90     98.23       2.72
Actual sol'n concentration:     99.59   mg/l   2.50 g soil
Average CPM of solution:     25933.60

************************************************************
Tube Set:    2    (1000 mg/l)                Tube 2      37205.50    914.90     161.35
                                               2.50 g soil
Concentration relative to stock:        0.020

C-14 spike:
  100.00 ul, added to           40.00 ml
                                             Tube 2D     37588.70    924.33     142.50
Actual sol'n concentration:    995.58   mg/l   2.50 g soil
Average CPM of solution:     40486.25

************************************************************
Tube Set:    3    (5000 mg/l)                Tube 3      41407.20   4878.48     198.56
                                               2.50 g soil
Concentration relative to stock:        0.100

C-14 spike:
  100.00 ul, added to           40.00 ml
                                             Tube 3D     37935.80   4469.49    1016.54
Actual sol'n concentration:   4977.76   mg/l   2.50 g soil
Average CPM of solution:     42249.85

************************************************************
Tube Set:    4    (10000 mg/l)               Tube 4      37681.30   9370.19    1170.56
                                               2.50 g soil
Concentration relative to stock:        0.200

C-14 spike:
  100.00 ul, added to           40.00 ml
                                             Tube 4D     40659.50  10110.78    -310.61
Actual sol'n concentration:   9955.48   mg/l   2.50 g soil
Average CPM of solution:     40034.95

************************************************************
Tube Set:    5    (25000 mg/l)               Tube 5      35826.70  23352.80    3071.67
                                               2.50 g soil
Concentration relative to stock:        0.500

C-14 spike:
  100.00 ul, added to           40.00 ml
                                             Tube 5D     36625.40  23873.41    2030.44
Actual sol'n concentration:  24888.64   mg/l   2.50 g soil
Average CPM of solution:     38182.90
************************************************************
```

```
SORPTION ISOTHERM SPREADSHEET FOR C14 DATA

PHENOL TO NATURAL ZEOLITE FROM METHANOL SOLUTION

Stock Solution Preparation:   50280.00 mg
                                 99.00% purity                             EQUILIBRIUM
                         in       1000 ml                         --------------------
Stock Solution :   49777.20 mg/l                           Liq      Liq       Sorbed
Solution Volume = 5.00 ml                                 Conc.     Conc      Conc
C-14 solution:        14.00 mg/l                        (cpm/ml)   (mg/l)    (mg/kg)

Equilibration Time:  8 Hours

**************************************************************
Tube Set:    6    (50000 mg/l)              Tube 6       37469.10  46114.45   7325.57
                                               2.50 g soil
Concentration relative to stock:         1.000

C-14 spike:
  100.00 ul, added to           40.00 ml
                                            Tube 6D      39271.50  48332.72   2889.02
Actual sol'n concentration:  49777.24   mg/l   2.50 g soil
Average CPM of solution:     40445.20
**************************************************************
```