

SORPTION OF ORGANIC MATERIALS BY
PURE CLAY MINERALS

By

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PREFACE

The results of experiments dealing with the sorption of organic acids by pure clay minerals are presented in this thesis. Experiments were binary, consisting of one sorbent and one sorbate, and were performed in a turbulent aqueous system. Variation in temperature and concentration of sorbent and sorbate was investigated in regard to the effect on sorption.

This research was based on ideas expressed by Professor Louis Hemphill in the summer of 1962. At that time, Professor Hemphill emphasized the need for study into the role of clay sorption as a method of partitioning organics in an aqueous environment,

The Author wishes to express his sincere appreciation to the following individuals and organizations:

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W. S. S.

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CHAPTER I

INTRODUCTION

1-1 Statement of the Problem

Clay minerals are widely distributed in nature and are common constituents in most natural water supplies. In fact a large portion of the turbidity in natural water supplies is due to clay minerals. One outstanding characteristic of clay minerals is their ability to sorb materials in an aqueous solution. The nature and extent of clay sorption is dependent upon the properties of the concentration and constituent fields through which the clay particles pass. In nature the properties of these fields are continually changing due to the sorbing and desorbing of organic and inorganic materials from the clay minerals.

Evaluation of the role clay turbidity plays in stream sanitation requires a study of limited variables in the laboratory and extension of these studies to realistic natural conditions by additional expanded experiments. This study is concerned with the design and analysis of realistic laboratory experiments which evaluate established theoretical relationships and formulate new relationships pertaining to the role of clay sorption in a natural water supply.

1-2 Scope of the Investigation

The purpose of this study is to evaluate the nature and extent of clay mineral sorption in simple aqueous systems. This study was

limited to experiments involving only sorbents, that which sorbs, and sorbates, that which is sorbed, in binary mixtures. Clay minerals commonly found in natural water supplies, montmorillonite, kaolinite, illite and halloysite were selected as the sorbents to be used in the study. Montmorillonite was chosen as the standard sorbent for the experimental work because of its abundance in nature and its sorption scavenging ability.

Sorbates selected were short-chain aliphatic organic acids, formic, acetic, propionic, butyric, iso-butyric and valeric acid. These aliphatic organic acids were selected for the study because they are common pollutants in natural water supplies, are waste products from microorganisms and are subject to analysis by conventional acidimetric methods. In the latter portion of the study, phenol an aromatic acidic material was used to evaluate the results of the study. Phenol was selected for the study because it is a common taste and odor contaminant as well as a standard material used to determine the effectiveness of activated carbon.

The effect on sorption by variation of environmental parameters was studied to a limited extent. Environmental parameters studied were temperature, concentration of the sorbate, and the concentration of the sorbent. Complexities arising from hydrological conditions, multi-exchange sorption reactions and simultaneous variations of environmental parameters renders the experiments naive in the evaluation of in situ clay mineral sorption. The experiments are indicative of the clay mineral sorption affinity for short chain organic acids in a simple aqueous system.

1-3 Historical

Adsorption was first observed in 1773 by Scheele in connection with the adsorption of gases by solids. ⁽¹⁾ Twelve years later Lowitz observed the adsorption of gases from solutions by charcoal. ⁽²⁾ The earliest systematic experiments on the adsorption of gases were carried out by T. de Saussure in 1814. ⁽¹⁾ It was not until 1875 that J. W. Gibbs placed the subject of sorption on a theoretical basis. ⁽¹⁾ Gibbs theorized that the concentration of substances at an interface will in general differ from those in the external phases. Until 1916 theories of sorption were concerned with a condensed liquid film or a compressed gas film on the surface of the sorbent. These films were believed to be relative thick with densities slowly decreasing as the distance from the interface increased. In 1916, I. Langmuir pointed out that the rapid decrease of intermolecular forces with distance indicates that the sorbed layer is probably only one molecule thick. ⁽³⁾ This view is now widely accepted for adsorption of gases on solids at low pressures and high temperatures. In 1938, Brunauer, Emmett and teller extended the original concepts of Langmuir to explain multilayer adsorption of gases, developing the famous B. E. T. theory of adsorption. ⁽⁴⁾ This theory is generally accepted and is the basis of the B. E. T. method for determining the surface area of powdered materials.

In the field of sanitary engineering sorption reactions have been used for a good many years. An early example in the use of sorption reactions is the slow sand filter. The organic matter passing through the slow sand filter is sorbed onto the "schmutzkecke" where it is stabilized by microorganisms. Sorption of organics by clays is not a new innovation to the field of sanitary engineering. In connection with the clarification of potable waters, it has sometimes been found

desirable to add a highly colloidal, easily dispersed clay to the water prior to addition of alum. (5) The clay collects colloidal material that would not otherwise settle and is in turn flocculated by the alum. (6) Slocum observed that the clays have a softening effect on water. (7) Weir stated that clays may also reduce the tastes and odors in water. (8) Wyoming Bentonites as well as Georgia and Florida Attapulgites have been extensively studied for use as clarification aids.

In connection with low level radioactive treatment processes, natural ion-exchange materials including clays have received extensive study. Results of this study have been used to improve the performance of the low-level radioactive waste treatment plant at Harwell, England and Oak Ridge, Tennessee. In both installations clay materials are used as a final treatment process to remove radionuclides from solution. (9)

Investigators in agriculture and the soil sciences have for many years realized the importance of clay organic complexes. In 1929 Demlin and Barrier showed a definite fixation of humic acid and protein by clay. (10) Since the early 1930's the clay-organic complexes and their reactions have been well established through continued development of X-ray diffraction and differential thermal analysis. Sorption characteristics for many non-aqueous organic systems have been studied. A systemized evaluation of this work appears in Grim's Clay Mineralogy. (11)

1-4 The Gibbs Equation

At an interface separating different compounds that are in the same or different phases sorption may occur. Sorption results from unsatisfied forces that exist at all interfaces. To a large extent, the most complex of sorption reactions are those occurring at a solid-

liquid interface. Gibbs formulated a quantitative relationship that is useful in solid-liquid interface and is a classic work in this field. Derivation of the Gibbs equation is presented in this study because it is the only theoretical expression for the sorption of liquids with respect to solids. A summary of the assumptions and restrictions made in the derivation are given at the end of the derivation.

The Gibbs free energy equation for a system composed of j components in one state is expressed as;

$$G = H - TS + \sum_{i=1}^j \mu_i n_i \quad (1-1)$$

The i th chemical potential is the inherent Gibbs free energy of one mole of the i th component in the system. Surface energy is usually considered to be zero and was therefore not considered in the above equation. In order to include the surface energy resulting from the surface area offered by a sorbant it is necessary to incorporate an expression for the surface energy into the Gibbs free energy equation. The surface energy of a system in a particular state is γA , where γ is the surface energy per unit area of sorbant and A is the total surface of the sorbant. Gibbs free energy can now be expressed as;

$$G = H - TS + \sum_{i=1}^j \mu_i n_i + \gamma A \quad (1-2)$$

Upon differentiation of the above equation the following equation is obtained for a change in the Gibbs free energy;

$$dG = SdT + VdP + \sum_{i=1}^j \mu_i dn_i + \sum_{i=1}^j n_i d\mu_i + Ad\gamma + \gamma dA \quad (1-3)$$

Considering a closed system where; the concentration of each of the components remains constant, the sorbent surface remains constant and the temperature and pressure do not change, it follows;

$$dG = \sum_{i=1}^j n_i d\mu_i + Ad\gamma \quad (1-4)$$

At equilibrium the change in the Gibbs free energy is zero. On setting dG equal to zero the following equation is obtained;

$$0 = \sum_{i=1}^j n_i d\mu_i + Ad\gamma \quad (1-5)$$

Limiting the above equation to a two component system, and eliminating that portion of the system not in the reactive neighborhood of an interface, the following equation can be deduced;

$$0 = n_1^{\circ} d\mu_1 + n_2^{\circ} d\mu_2 \quad (1-6)$$

This equation is known as the Gibbs-Duhem equation. In this equation n_1° is the number of moles of solute and n_2° is the number of moles of solvent, both in the liquid phase, n_1 is the number of moles of solute at the interface and n_2 is the number of moles of solvent at the interface. Multiplying the Gibbs-Duhem equation by n_1/n_1° , the following equation is obtained;

$$0 = n_1 d\mu_1 + n_1 n_2^{\circ} d\mu_2 / n_1^{\circ} \quad (1-7)$$

Subtracting equation 1-7 from equation 1-5 in which j is 2 gives rise to the following equation;

$$0 = n_2 d\mu_2 - n_1 n_2^{\circ} d\mu_2 / n_1^{\circ} + Ad\gamma \quad (1-8)$$

Rearranging the above equation;

$$- d\gamma/d\mu_2 = (n_2 - n_1 n_2^0/n_1^0)/A \quad (1-9)$$

In this equation the quantity $n_1 n_2^0/n_1^0$ is the fraction of n_2^0 associated with n_1 at the solid interface. Then $(n_2 - n_1 n_2^0/n_1^0)$ is the excess concentration of solute at the interface if the solute is considered as the sorbed material. This excess of solute at the interface is due to the solvent and solute surface energy being exerted at the interface. For a system to approach equilibrium the Gibbs free energy must trend toward a minimum. Free energy is given up by the system as it goes toward equilibrium and is used to retain up the solute at the interface.

Equation 1-9 quantitatively relates the excess concentration of solute per unit area of sorption surface. The right hand side of this equation may be denoted by Γ_2 , and is the surface concentration of solute per unit area of interface.

This consideration permits the following form;

$$\Gamma_2 = - \frac{d\gamma}{d\mu_2} \quad (1-10)$$

The chemical potential of a solute in a real system is expressed as follows;

$$\mu_2 = \mu_2^0 + RT \ln a_2 \quad (1-11)$$

where a_2 is the activity of the solute in the system and μ_2^0 is the chemical potential of the solute at standard temperature and pressure. Differentiating the above equation an expression for the change in the chemical potential of the solute is obtained as follows:

$$d\mu_2 = RT d \ln a_2, (dT = 0) \quad (1-12)$$

Substituting the above expression into equation 1-10 an equation in terms of the solutes activity is obtained as follows:

$$\Gamma_2 = - \frac{d\gamma}{RT \ln a_2} \quad (1-13)$$

or

$$\Gamma_2 = - \frac{d\gamma}{RT} \cdot \frac{a_2}{da_2} \quad (1-13a)$$

The above two equations are the forms in which the Gibbs equation is usually expressed. For very dilute solutions, the activity may be replaced by the concentration of the solute, giving rise to the following equation;

$$\Gamma_2 = - \frac{C_2}{RT} \cdot \frac{d\gamma}{dC_2} \quad (1-14)$$

Knowing the changes in the specific surface energy and the solute concentration, the above equation may be intergrated to determine the specific sorption Γ_2 .

The following assumptions and restrictions are made in the derivation of the Gibbs equation.

1. Constant Temperature. The sorption equations are sometimes referred to as isotherms.
2. The system is closed.
3. The interfacial area remains constant. In a turbulent system the size of clay particles will be reduced through attrition, therefore the total interfacial area will increase with increasing time.
4. The interface is considered fixed and the solute migrates toward it. This is not the case in a turbulent system.
5. No electrostatic forces are present. This is not the case with

electrolytic solutions. The Gibbs equation is insufficient to account for the sorption of electrolytes. It has been shown that the Gibbs equation is in agreement with the sorption of nonionizing liquids on solid interfaces. (12)

A solid's surface may sorb materials by virtue of molecular attraction from unsatisfied bonds and by providing an interface at which a solute that is capable of lowering the surface tension may accumulate. The Gibbs equation provides a theoretical basis for sorption of the latter type but is insufficient for ionic systems.

1-5 The Freundlich Isotherm

An expression that has been shown to agree with experimental sorption data for electrolytic solutes is the Freundlich isotherm, (13) It has generally been accepted as a model for the graphic presentation of liquid-solid interface sorption results although it does not possess a theoretical basis. Fair and Geyer present a method for evaluating threshold values of taste and odor contaminants through the use of Freundlich's isotherm. (14) Within recent years several theoretical derivations of Freundlich's isotherm have been presented for solid-gas interface sorption. (15) Freundlich's isotherm for a solid-liquid interface is still an empirical expression in which the constants are determined through experiment. A large portion of the results presented in this study are in the form of Freundlich isotherms.

The Freundlich isotherm is expressed as follows:

$$y/m = KC^n \quad (1-15)$$

where;

y is the amount of solute sorbed.

m is an extensive constant, the sorbent surface area or mass, and remains fixed during an experiment.

K is a constant that is a measure of the effectiveness of the sorbent.

n is an exponential constant relating the degree of sorption to the ratio of the concentration of sorbate to sorbent. In very high ratios, n approaches one, and the degree of sorption is linearly dependent upon sorbate concentration. In very low ratios, n approaches zero, and the degree of sorption is independent of sorbate concentration. This is the saturation value of the sorbate to sorbent ratio and it means that addition of excess sorbate will not produce additional sorption.

C is the amount of solute left in solution.

The condition of saturation is not realized from a plot of a Freundlich isotherm and therefore, must be considered separately. A good example of saturation at a gas-solid interface is the Brunauer's Type I physical adsorption curve shown in figure 1-1. (16)

The amount of gas sorbed increases as pressure increases to a limit, P_s . The saturation pressure, P_s , is that pressure above which an increase in pressure will not increase the amount of gas sorbed. There are no standard curves for liquid-solid sorption depicting saturation; however, the liquid-solid system can be considered analogous to Brunauer's Type I gas-solid system by equating the concentration of the liquid sorbate to the pressure of the gas.

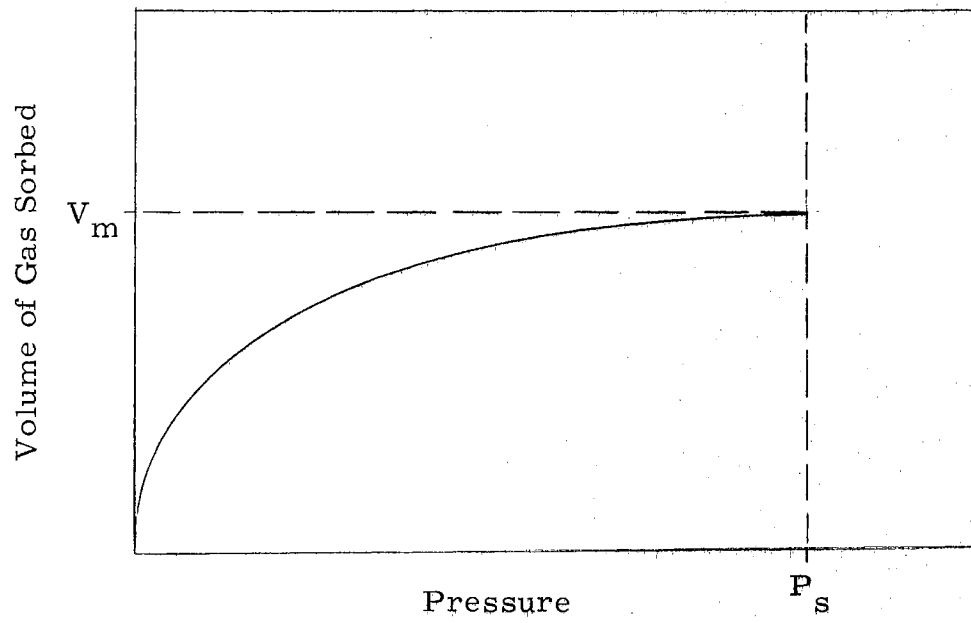


Fig. 1-1

Unimolecular Adsorption of a
Gas Film

CHAPTER II

METHODS AND MATERIALS

2-1 Clay Minerals

The sorbents selected for this study were pure clay minerals and activated carbon. The clay mineral samples selected are representative of naturally occurring species of clay and represent two major clay crystalline systems. Samples of pure montmorillonite, kaolinite, illite and halloysite clay minerals were obtained from Wards Natural Science Establishment. The purity of the clay mineral samples were established by Dr. Ralph J. Holmes, Columbia University, under the auspices of the American Petroleum Institute Clay Mineral Project No. 49. The locations from which the clay samples were taken are listed in Table (2-1), along with the assigned American Petroleum Institute, API, numbers.

TABLE 2-1

CLAY MINERAL SAMPLES

Clay Mineral API No.	Geographical Location
Montmorillonite No. 21 (Bentonite)	Chrisholm Mine, Polkville, Miss.
Kaolinite No. 2	Birtch Pit, Macon, Georgia
Halloysite No. 29	Wagon Wheel Gap, Colorado
Illite No. 36	Morris, Illinois

In general, the clay minerals are similar in chemical composition. This can be seen from Table (2-2) in which the composition of the clay minerals used in this study are listed. The major difference between the compositions of the clay minerals is the amount of magnesium, potassium, aluminum, calcium and sodium oxides in the clays.

As with organic compounds, the structure of the clay minerals are responsible for many of the physical properties and chemical affinities of the clays. The demonstrated relationships between the structure of the clay minerals and physiochemical properties are a recent development. Since the development of X-ray diffraction techniques, the shape and structure of clay minerals have become increasingly well defined. X-ray diffraction data is frequently used as a method of identification of clays with considerable similarity. Through the application of this technique a shift in the structural spacing of clays due to thermal energy, element substitution and sorption of organics can be measured. In 1934 a variation in the "c" axis spacing of montmorillonite following sorption of an organic was detailed by Hofmann through use of X-ray diffraction. (17)

The shape and size of clay particles has been determined from electron micrographs. Electron micrographs of the clays do not show the true size and shape of the clays due to the high energy to which the sample is subjected and distortion produced by vacuum dehydration. In spite of these shortcomings, the electron microscope method provides an excellent method for comparing the size and shape of clay particles. Comprehensive evaluation of the electron micrographs of the four clay minerals, montmorillonite, kaolinite, illite, and halloysite, show the relative size and shapes of the particles. The clay samples used in

TABLE 2-2

CHEMICAL ANALYSIS OF SOME CLAYS

% COMPOSITION

Oxide Clay	Mont. (20)	Kaol. (21)	Hall. (21)	Illite (22)
SiO ₂	50.20	45.20	43.98	52.23
Al ₂ O ₃	16.19	37.02	38.46	25.85
Fe ₂ O ₃	4.13	0.27		4.04
FeO		0.06	0.03	
MgO	4.12	0.47	TR	2.69
CaO	2.18	0.52	0.32	0.60
K ₂ O	0.16	0.49	0.48	6.56
Na ₂ O	0.17	0.36	0.14	0.33
TiO ₂	0.20	1.26	0.01	0.37
H ₂ O-	15.58	1.55	2.58	
H ₂ O+	7.57	13.27	14.59	7.88
TOTAL	100.50	100.47	100.59	100.55

this study, selected prototypes, have been examined and detailed by electron microscopy. (18)

Electron micrographs of montmorillonite show it to consist of extremely small particles approaching as a lower limit 0.002 microns in diameter. Detailed structure and shape of the individual particles are not apparent in the micrographs; the particles are usually conglomerated together and appear as an irregular fluffy mass.

Electron micrographs of the clay mineral kaolinite show it to consist of six-sided flakes with a frequent prominent elongation in one direction. The maximum arial dimensions are from 0.3 to 4 microns with a thickness of from 0.05 to 2 microns.

Illite flakes are shown, from electron micrographs, to have an irregular well defined outline of uniform thickness. (19) The diameter of the flakes is from 0.1 to 0.3 microns. Shape of the illite particles resemble those of some montmorillonites except that the particles of illite are larger, thicker and have well defined edges.

Electron micrographs of halloysite show the particles to be long hollow tubes ranging in length from 0.3 to 3 microns with an average diameter of 0.07 microns. Bates believes that the halloysite tubes are made up of thin curled up sheets, the curling being due to strains formed by a misfit between the silicon-oxygen layer and the aluminum-hydroxyl layer. (19)

The structures of clay minerals are well defined lattice configurations deduced from X-ray diffraction studies. Most clay minerals consist of two basic structural units, a silica tetrahedron and a lattice composed of two layers of closed packed oxygens or hydroxyls with atoms of an alkali earth filling the octahedral, dioctahedral or trioctahedral lattice

positions. A sketch of these basic structural units is shown in figure (2-1).

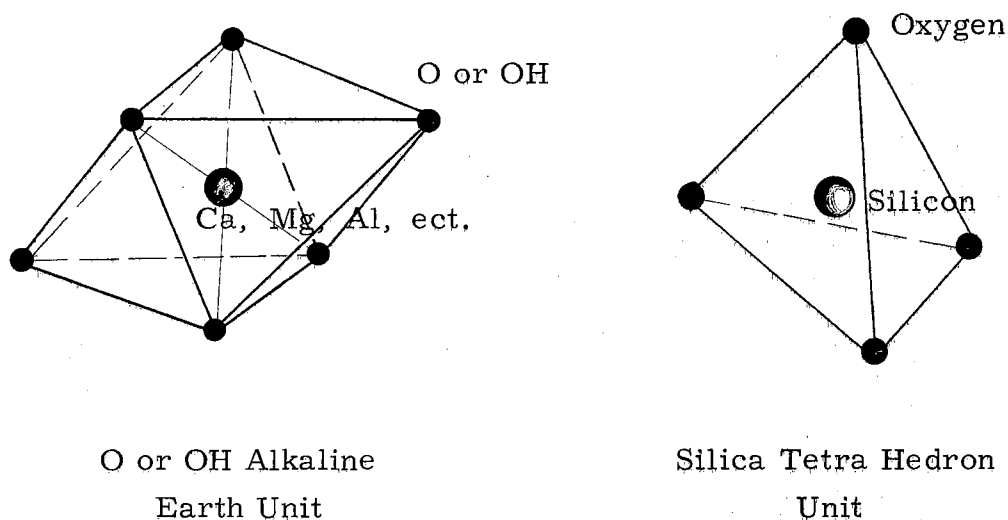


Fig. 2-1

Basic Structural Units of Clay Minerals

The silica tetrahedral units form sheets by arranging themselves into a hexagonal array, as shown by a plan view in figure (2-2). The oxygen or hydroxyl alkaline earth units arrange themselves in a sheet so that the top and bottom of the sheet are closed packed arrays of oxygens or hydroxyls. Alkaline earth atoms are interspersed between the top and bottom of the sheet in octahedral, dioctahedral or trioctahedral lattice positions.

Clay minerals are classified according to their structure.

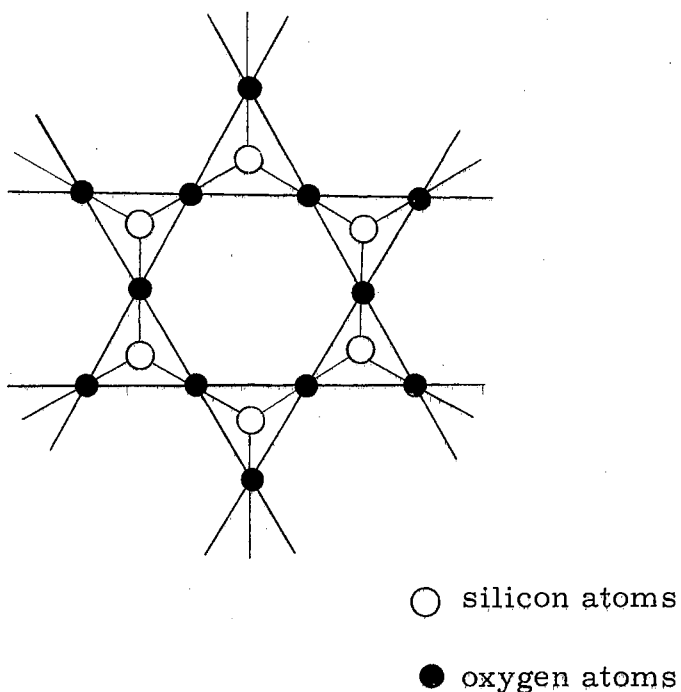


Fig. 2-2

Plan View of a Silica
Tetrahedron Sheet

Montmorillonite is classified as a crystalline, three layer sheet structure composed of two layers of silica tetrahedrons and one central dioctahedral, two-thirds of the octahedral positions are filled, or trioctahedral, all of the octahedral positions are filled, layer, equidimensional expanding lattice structure. Illite clay mineral is similar in structure to montmorillonite except that its lattice is non-expanding. Halloysite is classified as a crystalline, two layer sheet structure composed of one layer of silica tetrahedrons and one layer of alumina octahedrons, elongate lattice structure. Kaolinite is similar in structure to halloysite except that its lattice structure is equidimensional.

Montmorillonite and halloysite clay minerals have a unique char-

acteristic, they sorb organic materials between their unit layers. One investigator showed that montmorillonite and halloysite may form in their structures an interfacial sorbed layer of organic material several molecules thick. ⁽²³⁾ Other clay minerals such as illite and kaolinite, which do not have an expanding lattice, are limited to external surface sorption.

In Table 2-3, ion-exchange capacity, maximum molecular depth for interfacial sorption, "c" axis for clay minerals as they naturally exist, and specific surface area values are listed for the four clay minerals used in this study. Generally, as suggested by the data in Table 2-3, the clay minerals ability to sorb organic materials between their unit layers increases with an increase in the thickness of the unit clay particle, "c" axis spacing. This can be explained from a consideration of the thickness of the sorbed water layer that exists between the unit layers of most clay minerals. The ease with which an organic material replaces the sorbed water layer is dependent upon the mobility or viscosity of the water in this layer. As a particle of water approaches the surface of a clay particle the viscosity of the water increases due to the coulombic forces of attraction that increase with decreasing distance from the clay particle. With an increased thickness in the sorbed water layer, it can be seen that the central region of the layer becomes less viscous due to its increased displacement from the clay particle and is, therefore, more easily displaced by an organic material. The thickness of the unit layers for montmorillonite and illite are equal as is the thickness of the unit layers for kaolinite and halloysite. There exists, however, a discrepancy in the "c" axis spacing of 5.5 Å[⊖] between montmorillonite and illite and 2.87 Å[⊖] between halloysite and kaolinite. This

TABLE 2 - 3

STRUCTURAL PROPERTIES OF THE CLAY
MINERALS STUDIED

Clay Mineral	Ion Exchange Capacity (meg/100g)	Max. Molecular Depth for Inter-Layer Sorption	"c" Axis Spacing (Å)	Specific Surface Area (M ² /g at 30° C.)
Montmorillonite	80 - 150	3	15.5	15.5
Kaolinite	3 - 15	0	7.38	15.5
Illite	10 - 40	0	10 approx.	97.1
Halloysite	40 - 50	1	10.25	43.2

excess in thickness for montmorillonite and halloysite is the additional thickness in their sorbed water layers over those of illite and kaolinite. This accounts for the fact that montmorillonite and halloysite sorb between their unit layers whereas kaolinite and illite do not.

From the data presented in Table 2-3, it is obvious that neither ion exchange capacity nor molecular depth of interfacial sorption are dependent upon the specific surface of the clays. The type and strength of the unsatisfied forces at the surface of a clay particle and its ability to sorb between its unit layers is more indicative of a clay's performance.

Clay minerals are widespread in nature and are complex in their functions and structure. Most clay minerals are structurally similar but have different sorption characteristics. These characteristics are dependent upon the strength and type of the unsatisfied forces both interior and exterior to the clay particle. Sorbed water depth between unit layers of a clay mineral govern whether a clay can sorb materials between its unit layers.

2-2 Organic Materials

The organic materials used in this study were six aliphatic carboxylic acids, formic, acetic, propionic, butyric, isobutyric and valeric, and one aromatic enol, phenol. Straight chained acids were selected as the sorbates for the study because they are natural materials produced by water borne organisms, have a well defined structure, are similar in structure for comparison and are subject to analysis by conventional acidimetric methods. The normal carboxylic acids are related in that they have a single carboxylic group with a variable length hydrocarbon residue. This relationship provides a basis for

studying similar materials having different sizes. In addition to the normal carboxylic acids, formic, acetic, propionic, butyric and valeric, an iso form, isobutyric, was studied to determine the effect on sorption from a change in molecular symmetry. One sorption experiment was conducted using phenol, an aromatic acid, to compare the difference in sorption characteristics between an aromatic acid and the aliphatic, carboxylic acids.

The physical and chemical properties of the low membered carboxylic acids and phenol are listed in Table 2-4. The values listed in Table 2-4 show that water solubility and vapor pressure (at 100° C) vary inversely with the maximum dimension of the carboxylic acids. It can also be seen that the boiling point of all the acids varies with their molecular weight. Isobutyric acid approaches propionic acid in its properties. This is probably due to the fact that both of the acids have the same maximum dimension. An interesting characteristic of the normal carboxylic acids, as shown by the melting point data in Table 2-4, is the variation in the melting points of the acids. Normal carboxylic acids with an even number of carbon atoms always melt at a higher temperature than do the next higher acids. All of the carboxylic acids with less than six carbon atom chain are soluble in water. The lower member acids, formic, acetic and propionic exhibit a sharp acrid taste and odor, whereas; butyric, isobutyric and valeric acid produce a severely disagreeable taste and odor.

The organic acids possess a large dipole moment. This property plus the possibility of hydrogen bonding between the acid molecules in an aqueous media permits dimer formation. Upon the formation of a dimer, the double acid molecule loses its dipole moment. With decreasing acid concentration, dimer formation is reduced. Acetic acid

TABLE 2 - 4

PROPERTIES OF CARBOXYLIC ACIDS AND PHENOL

Acid	# of Carbon Atoms	Molecular Weight	Maximum Dimension in Å	Boiling Point (° C)	Melting Point (° C)	Water Solubility (g/100ml)	Vapor Pressure at 100° C in (mm Hg)	$K_i \times 10^{-5}$ at 20° C.
Formic	1	46.03	3.49	100.7	8.40	Miscible	753	17.700
Acetic	2	60.05	5.03	118.2	16.60	in all	417	1.753
Propionic	3	74.08	6.57	141.4	-22.00	Proportions	183	1.340
Butyric	4	88.10	8.11	164.1	- 7.90	5.62	70	1.506
Isobutyric	4	88.10	6.57	154.5	-19.00	20.00	100	1.550
Valeric	5	102.13	9.65	184.4	-34.50	3.70	28	1.560
Phenol	6	94.11	aromatic	182.0	41.00	6.70	40	4.16×10^{-2}

exhibits the property of dimer formation to a larger degree than do the other acids. Bradely states that polar molecules may be sorbed by clay minerals, especially montmorillonite, between the unit layers of the clays and are held through a C - H ---- O (clay-mineral surface) bond.⁽²⁴⁾ The possibility of sorption of the acid molecules by clay minerals due to the acids being dipoles is explored in the experimental results.

Many water borne organisms have the ability to produce organic acids through anaerobic fermentation of sugars and related materials. A number of bacteria, particularly those belonging to the family Enterobacteriaceae, carry out so-called formic fermentations in which formic acid is produced either as an end product of sugar metabolism or an intermediate metabolite. Fermentation by Escherichia coli produces formic acid that is further decomposed by an enzyme system known as formic hydrogenlyase to yield CO₂ and hydrogen. Salmonella typhi do not possess the hydrogenlyase system and produces formic acid as an end product. Escherichia coli and Aerobacter aerogenes both produce acetic acid as an end product in sugar fermentation. Propionic acid bacteria of the genus Propionibacterium produce propionic and acetic acid in sugar and lactic acid fermentations. Several groups of obligate anaerobic bacteria are characterized by the ability to produce butyric acid in the fermentation of sugars and related substances. Certain species of the genus Clostridium produce, through sugar fermentation, butyric as well as acetic acid as end products.⁽²⁵⁾

2-3 Methods of Analysis

The development of a method for measuring the degree of sorption of organic acids by pure clay minerals was accomplished by experiment. The degree of sorption was determined by analyzing for the sorbate

remaining in solution after sorption.

Preliminary to the analysis of the sorbate remaining in solution a separation technique must be employed to remove the sorbent and its sorbed sorbate from solution. The criteria for this technique were 1) separation of an aqueous solution from a solid sorbent must not influence the distribution of sorbed sorbate with respect to solution phase sorbate, 2) separation should be rapid, not involving an atypical distribution of sorbent. Filtration was found to be an unsatisfactory separation method because the filter was immediately clogged by the clay particles. Further laboratory investigation showed that clay slurries contacted with organic acids for extended periods of time failed to show any sorption when an aliquot of the entire mixture was analyzed; however, sorption was detected when the clear solution was sampled after the clay had settled. This observation suggested separation by centrifugation. Additional study showed that centrifugation was a convenient reproducible method for separation. The separation scheme established by this study is detailed as follows:

Samples to be analyzed were first separated by centrifugation at 2000 rpm for 40 minutes in a centrifuge with a 15 inch diameter head. Centrifugation at the above rate, according to Stokes law, would cause a spherical particle 0.0875 microns in diameter to travel 15 cm. in water at 20° C. The length of a centrifuge tube was 15 cm. and the lower limit in size of the clay particles, those of montmorillonite, is 0.002 microns. Particles of clay smaller than an effective size of 0.0875 microns were believed to constitute only a small portion of the clays. This is based on the fact that when the samples were centrifuged at the above values, the supernate was visually clear with no pinpoints of light existing, a characteristic of colloidal clay particles.

Experimental procedure for the determination of the degree of sorption was as follows. Open system samples of clay and acid were mixed by means of a conventional six place laboratory stirrer in one liter pyrex glass beakers. Closed system samples were mixed in glass stoppered one liter flasks by magnetic stirrers. The volume of all the samples was 900 ml. Sample solutions were mixed at a constant rate and sampled at frequent intervals. The sample aliquots were centrifuged. The supernatant was then drawn off and analyzed for acid concentration. The acid concentration in the supernate represented the concentration of acid remaining in the sample solution phase. The difference between the initial acid concentration in the sample and the acid concentration remaining in the samples solution phase after some time is the amount of acid sorbed during an elapsed time. A basic expression giving the fraction sorbed is then;

$$\Theta_{\text{sorb}} = \frac{C_0 - C(t)R}{C_0} \quad (2-1)$$

in which Θ_{sorb} is the fraction sorbed, C_0 is the initial concentration or sorbate in solution, $C(t)$ is the concentration of sorbate in solution after some time t and R is a control correction factor.

Analysis of the carboxylic acids was by acidimetric titration using the following procedure. Ten milliliters of the centrifuged supernate and 25 ml. of distilled water were placed in a 50 ml. pyrex glass beaker and titrated with 0.02 N. NaOH to an end point of pH 7.0 with a pH meter. The concentration of acid left in the solution phase of the sample in meq/l is represented by the ml. of NaOH used to titrate the supernate times two, a conversion factor derived from $V_1N_1 = V_2N_2$. Centrifuged supernatant from the aliquots of phenol samples were analyzed

for phenol concentration by a modified 4- aminoantipyrine colormetric method. (26, 27) This method is accurate for determining phenol concentrations greater than 1ppm. The basis of the method is that phenol and 4- aminoantipyrine complex in the presence of the oxidizing agent, potassium ferricyanide, at a pH of 10 to yield a yellow color. The color intensity of this solution follows Beers law. In laboratory practice the percent transmission of light through the prepared sample was measured in a spectrometer at 510 mu. The percent transmission value was referenced to a previously prepared calibration curve to determine the phenol concentration.

Prior to laboratory application, each of the clay minerals was desiccated at ambient temperature until constant weight was obtained. Samples of the clays were measured out by weighing on an analytical balance. Clays were not heated to obtain constant weight because they are subject to severe irreversible structural changes, especially halloysite, at relatively low temperatures. (28)

In all the experiments, controls were used to evaluate the changes in sorbate concentration not attributable to sorption. Controls for the open system carboxylic acid experiments were used to determine the changes in acidity due to clay acidity and acid volatilization and consisted of 1) carboxylic acid in distilled water, and 2) clay mineral in distilled water. Closed system carboxylic acid experiments were adjusted for clay acidity only. Experiments involving phenol as the sorbate were adjusted for changes in phenol concentration not attributable to sorption through use of phenol distilled water control experiments.

Experimental results for the carboxylic acids were directly corrected for clay acidity by subtracting from an experimental acidity

value the clay acidity value of corresponding clay concentration and elapsed time. Experimental open system results were further corrected for loss of acid through volatilization.

In the adjustment of experimental results for acid loss through volatilization, it was first assumed that sorbed acid cannot exert a vapor pressure on the solution and, therefore, cannot be lost due to volatilization. This is actually an adjustment on the control by the experiment. An expression for the adjustment of experimental results for acid loss through volatilization is

$$\Theta_{\text{sorb}_t} = \frac{C_0 - C(t)(1 + \Theta_{c_t})}{C_0} \quad (2-2)$$

In which Θ_{sorb_t} is the corrected fraction of sorbate sorbed at an elapsed time t , C_0 is the initial experimental acid concentration, $C(t)$ is the experimental acid concentration in solution at an elapsed time t and Θ_{c_t} is the fraction of acid lost in the control at an elapsed time t . The use of the assumption that sorbed acid is not volatilized is seen in Eq. 2-1 as the subtraction of $C(t) \Theta_{c_t}$, instead of $C_0 \Theta_{c_t}$, from C_0 . The expression $(1 - \Theta_{c_t})$ is R , the control correction factor in Eq. 2-1.

CHAPTER III

EXPERIMENTS

3-1 Isotherm Experiments

Isotherm experiments were conducted in accordance with the Freundlich isotherm requirements. In this study the clay concentration was fixed while the acid concentration was varied. The experiments were conducted at ambient temperature, 26° C., in closed and open containers. All solutions and slurries were mixed at 60 rpm throughout the experiment. Isotherms were developed for the sorption of the carboxylic acids, acetic, formic, and butyric and the enol, phenol by montmorillonite and for the sorption of acetic acid by illite.

Controls were used to correct for clay acidity of the clay minerals illite and montmorillonite. These controls were evaluated by measuring the rate of change in acidity or alkalinity produced in a well mixed solution of clay and distilled water. All the experiments were conducted in closed vessels, with the exception of the acetic acid and montmorillonite experiment, and therefore eliminated the need for correction of experimental results for acid loss from volatilization.

Freundlich isotherms were developed from the experimental results by plotting the ratio of the amount of sorbate sorbed per unit sorbate left in solution, for specific contact times. The data for the isotherms was used to determine a straight line on log-log paper by a modified method of least squares. A sample calculation of this method appears in Appendix B. The experimental results are presented at the

end of this section in the form of Freundlich isotherms. Comparisons of the isotherms and conclusions as to the relative sorption characteristics of the sorbates and sorbents, studied, are listed in section 3-1F.

A. Montmorillonite and Acetic Acid

This experiment was conducted in an open turbulent system. The concentration of the clay mineral montmorillonite was held to a constant 1110 mg/1 while the concentration of the acetic acid was varied from 88 meq/1 to 700 meq/1. Pilot experiments, conducted with acetic acid and distilled water, showed that the loss in acidity from these acid controls was less than the variation in the experiment. The experimental results were, therefore, not corrected for loss in acetic acid through volatilization. Correction for clay acidity, from the montmorillonite clay acidity control curve in figure 3-1, was also insignificant when compared to the magnitudes of the acetic acid concentrations studied in this experiment. Experimental results are tabulated in Table 3-1. Isotherm data prepared from the experimental results in Table 3-1 is also tabulated in Table 3-1.

B. Montmorillonite and Formic Acid

This experiment was conducted at ambient temperature, 26° C, in a closed turbulent system, with the concentration of montmorillonite held to a constant 1220 mg/1 and the concentration of acetic acid varied between the limits of 2.92 meq/1 to 121.1 meq/1. The experimental results were corrected for clay acidity through use of a clay acidity control, for montmorillonite. This control consisted of 1220 mg/1 of montmorillonite in distilled water. A clay acidity correction curve was prepared by plotting the acidity in meq/1 of montmorillonite against

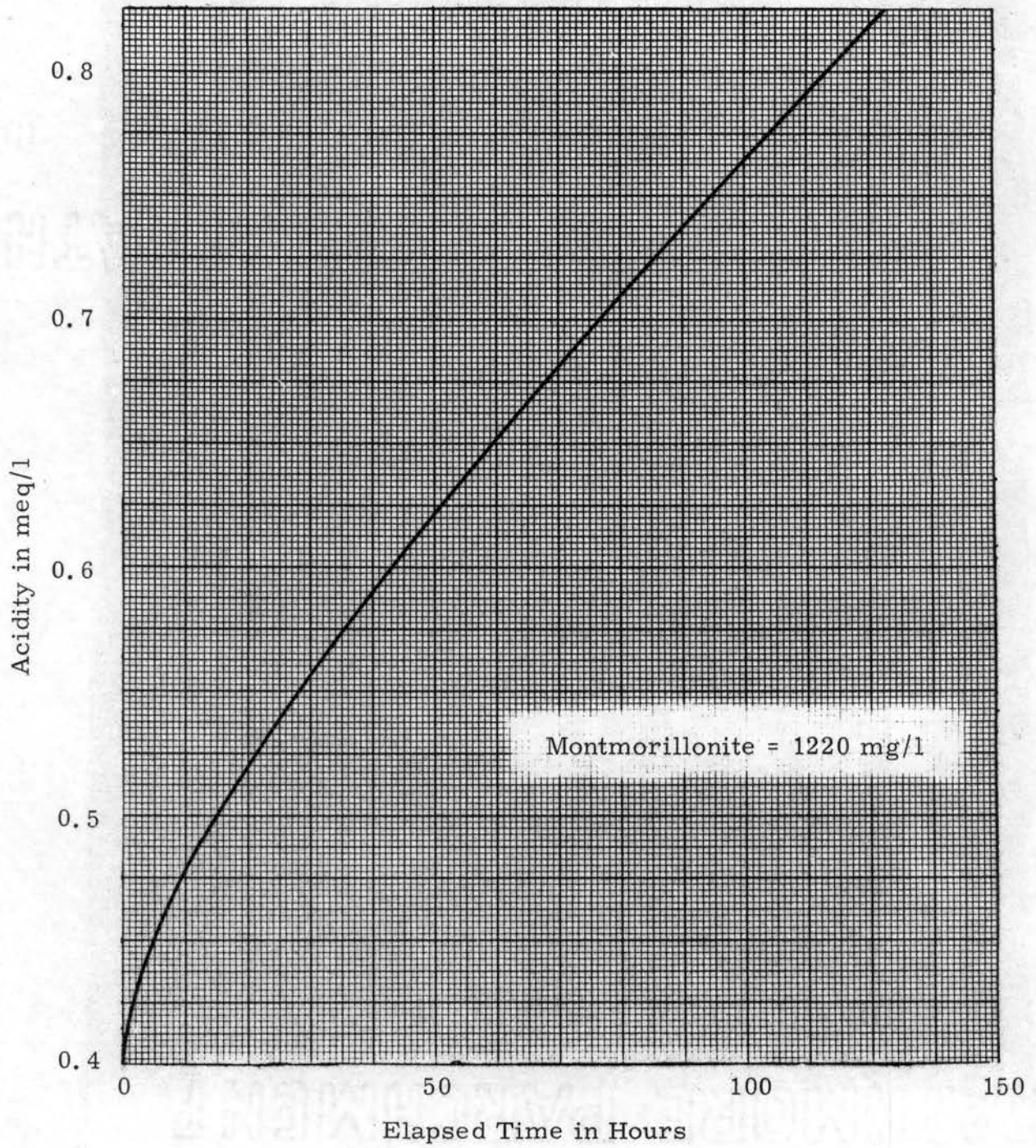


Fig. 3-1

Montmorillonite Clay Acidity
Control Curve

corresponding elapsed time, from Table 3-2, and is presented in Figure 3-1. Experimental results, both corrected and uncorrected for clay acidity, are tabulated, along with respective elapsed times, in Table 3-3. Isotherm data prepared from the corrected experimental results, from Table 3-3, appears in Table 3-4.

TABLE 3-1

EXPERIMENTAL SORPTION DATA AND ISOTHERM DATA
FOR ACETIC ACID AND MONTMORILLONITE

Sample #	Clay Conc. (mg/l)	Experimental Sorption Data		Isotherm Data at 24 Hours		
		Initial	24 Hours	y(sorbed)	C(in soln.)	y/m x 10 ³
1	1110	88	78	10	78	9.01
2	1110	168	148	20	148	18.02
3	1110	318	278	40	278	36.04
4	1110	474	414	60	414	54.05
5	1110	700	600	100	600	90.09

TABLE 3-2

MONTMORILLONITE CLAY ACIDITY CONTROL DATA

Clay Conc. (mg/l)	Acidity in meq/l				
	Initial	6	24	36	72
Elapsed Time					
1220	0.04	0.46	0.54	0.57	0.68

TABLE 3 - 3

CORRECTED AND UNCORRECTED EXPERIMENTAL SORPTION DATA
FOR FORMIC ACID AND MONTMORILLONITE

Sample Clay # Conc. (mg/l)		Experimental Data Uncorrected for Clay Acidity					Experimental Data Corrected for Clay Acidity				
		Initial	6	24	36	72	Initial	6	24	36	72
1	1220	2.92	2.64	2.36	2.37	2.52	2.52	2.18	1.82	1.80	1.84
2	1220	5.90	5.36	5.24	5.22	5.38	5.50	4.90	4.70	4.65	4.70
3	1220	10.90	10.70	10.60	10.50	10.40	10.50	10.24	10.06	9.93	9.82
4	1220	19.40	18.40	17.70	17.50	17.60	19.00	17.94	17.16	16.93	16.92
5	1220	36.00	34.40	34.20	34.00	34.30	35.60	33.94	33.66	33.43	33.62
6	1220	121.10	119.80	119.00	117.70	118.00	120.70	119.34	118.46	117.14	117.32

TABLE 3-4

ISOTHERM DATA FOR FORMIC ACID AND
MONTMORILLONITE

Sample Clay # Conc. (mg/l)	(y) Acid sorbed in meq/l			(C) Acid Remaining In Solution In meq/l			(y/m) Acid Sorbed in meq/l Over Clay Conc. in mg/l		
	24	36	72	24	36	72	24	36	72
1 1220	0.70	0.72	0.68	1.82	1.80	1.84	0.574	0.591	0.557
2 1220	0.80	0.85	0.80	4.70	4.65	4.70	0.656	0.696	0.656
3 1220	0.44	0.57	0.68	10.06	9.93	9.82	0.361	0.466	0.557
4 1220	1.84	2.07	2.08	17.16	16.93	16.92	1.510	1.700	1.710
5 1220	1.94	2.17	1.98	33.66	33.43	33.62	1.590	1.780	1.620
6 1220	2.24	3.56	3.38	118.46	117.14	117.32	1.840	2.920	2.770

C. Montmorillonite and Butyric Acid

This experiment was conducted at ambient temperature, 26° C., in a closed system. The concentration of the butyric acid was varied from 2.76 meq/l to 109.9 meq/l with the concentration of montmorillonite held to a constant 1220 mg/l. The experimental results were corrected for clay acidity from the montmorillonite clay acidity control curve in Figure 3-1. Experimental results, both corrected and uncorrected for clay acidity, are tabulated in Table 3-5. Isotherm data prepared from the corrected experimental results is tabulated in Table 3-6.

D. Montmorillonite and Phenol

This experiment was conducted at ambient temperature, 26° C., in a closed turbulent system. Concentration of the phenol was varied from 0.5ppm to 4.0ppm with the concentration of montmorillonite held to a constant 318 mg/l. The experimental results were obtained from analyzing the samples from time to time using a modified 4-aminoantipyrine colormetric method. Control experiments were used to minimize any day to day variations in the colorimeter. The experimental results were obtained in the form of percent transmission data, being converted to ppm phenol data through use of the colormetric calibration curve in Figure 3-2. The results were further converted to meq/l of phenol. The experimental results are tabulated in Table 3-7.

E. Illite and Acetic Acid

This experiment was conducted at ambient temperature, 26° C., in a closed turbulent system, with the concentration of illite held to a constant 1110 mg/l and the concentration of acetic acid varied between the limits of 3.13 meq/l to 20.0 meq/l. The experimental results were

TABLE 3-5

CORRECTED AND UNCORRECTED EXPERIMENTAL SORPTION DATA
FOR BUTYRIC ACID AND MONTMORILLONITE

Sample #	Clay Conc. (mg/l)	Experimental Data Uncorrected for Clay Acidity				Experimental Data Corrected for Clay Acidity			
		-----MEQ/L-----							
Elapsed Time In Hours		Initial	3	19	.60	Initial	3	19	.60
1	1220	2.76	2.54	2.44	2.34	2.36	2.09	1.92	1.69
2	1220	5.36	5.16	5.02	4.95	4.96	4.71	4.50	4.30
3	1220	10.00	9.85	9.74	9.69	9.60	9.40	9.22	9.04
4	1220	17.80	17.60	17.60	17.40	17.40	17.15	17.08	16.75
5	1220	33.20	32.40	32.20	31.80	32.80	31.95	31.68	31.15
6	1220	67.50	67.30	66.60	66.40	67.10	66.85	66.08	65.85
7	1220	109.90	109.30	109.30	109.10	109.50	108.85	108.78	108.45

TABLE 3-6

ISOTHERM DATA FOR BUTYRIC ACID
AND MONTMORILLONITE

Sample #	Clay Conc. (mg/l)	(y) Acid Sorbed in meq/l.		(C) Acid Remaining in Solution in meq/l.		$(y/m) \times 10^3$ Acid sorbed Over Clay Conc. (in mg/l) in mg/meq.	
		19	60	19	60	19	60
1	1220	0.44	0.67	1.92	1.69	0.360	0.550
2	1220	0.46	0.66	4.50	4.30	0.377	0.541
3	1220	0.38	0.56	9.22	9.04	0.312	0.459
4	1220	0.32	0.65	17.08	16.75	0.262	0.533
5	1220	1.12	1.65	31.68	31.15	0.919	1.352
6	1220	1.02	1.25	66.08	65.85	0.836	1.025
7	1220	0.72	1.05	108.78	108.45	0.590	0.861

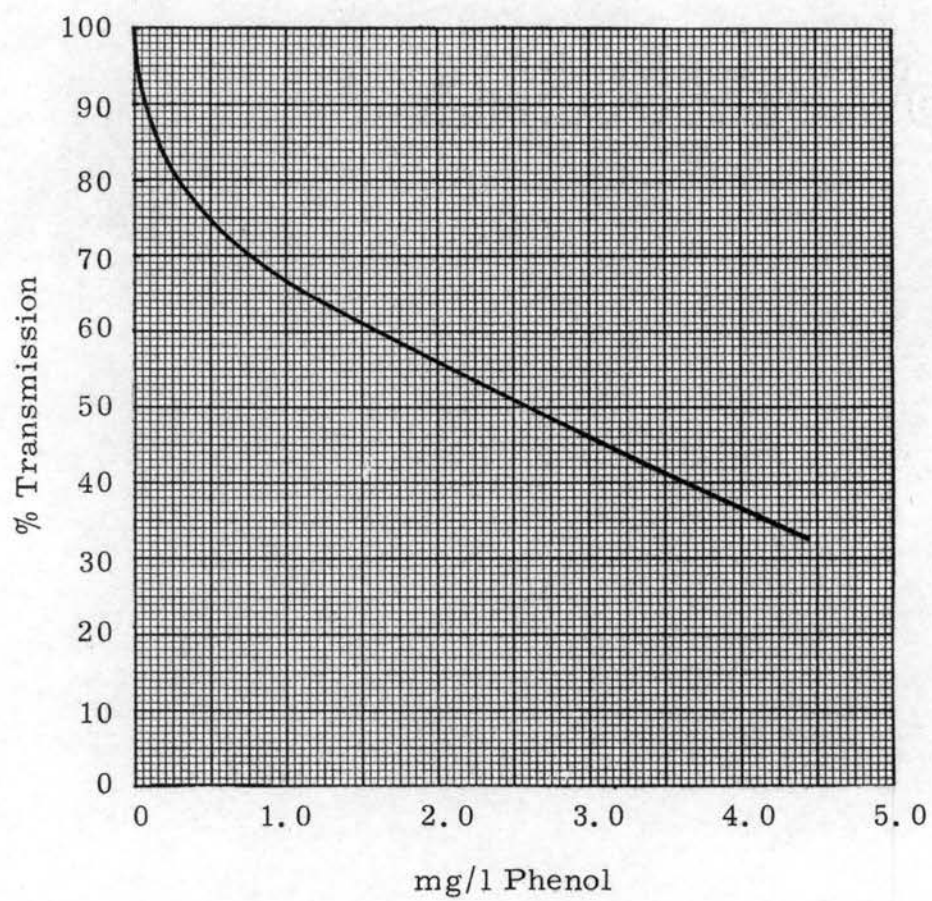


Fig. 3-2

Calibration Curve for Phenol Using Modified
4-Aminoantipyrine Colormetric Method

TABLE 3-7

EXPERIMENTAL SORPTION DATA AND ISOTHERM DATA FOR PHENOL
AND MONTMORILLINITE

Sample #	Clay Conc. (mg/l)	Percent Transimission		Phenol Conc. in mg/l		Phenol Conc. in meq/l x 10 ³		Isotherm Data		
		Initial	135	Initial	135	Initial	135	(y)	(C)	(y/m)
Elapsed Time in Hours		all x 10 ³ Phenol Sorbed, in Soln. at 135 hours								
Control	318	59.2	60.0	1.68	1.62	--	--	--	--	--
1	318	74.3	95.4	0.50	0.03	5.41	0.32	5.09	0.32	0.016
2	318	66.2	92.8	1.00	0.05	10.62	0.54	10.08	0.54	0.034
3	318	56.7	75.5	2.00	0.42	21.24	4.46	16.78	4.46	0.053
4	318	36.8	55.5	4.00	2.08	42.48	22.10	20.38	22.10	0.064

corrected for clay acidity due to illite through the use of illite clay acidity controls. The controls were evaluated by measuring the change in alkalinity or acidity produced by adding the clay to a well mixed solution of distilled water. These controls were analyzed with respect to time and clay concentration. The experimental results of the illite clay controls are shown in Table 3-8. Values for illite clay acidity in meq/l, from Table 3-8, were plotted against corresponding illite concentrations in mg/l to produce the curves for clay acidity vrs. clay concentration in Figure 3-3. A straight line of best fit was plotted through the data corresponding to initial, 24 and 44 hours elapsed time using a statistical method of least squares, see Appendix A. A curve of best fit was drawn through the points corresponding to 69 hours elapsed time. The curves in Figure 3-4 were derived from the curves in Figure 3-3 by plotting clay acidity against elapsed time for particular clay concentrations. The experimental sorption data was corrected for clay acidity by subtracting from the experimental acidity corresponding to the same concentration and elapsed time. The experimental sorption data, corrected and uncorrected for clay acidity, is tabulated, along with the respective elapsed time, in Table 3-9. Isotherm data was prepared from the corrected experimental results in Table 3-9 and is tabulated in Table 3-10.

F. Comparison of Isotherms

The Freundlich isotherms in Figure 3-5, show that sorption of organic acids by montmorillonite is variable as to acid type. The degree of sorption of acetic acid at higher concentrations, greater than 7 meq/l of acid remaining in solution, by montmorillonite was greater than by illite. Acetic acid, in the higher concentrations, was sorbed to a

TABLE 3-8

ILLITE CLAY CONTROL DATA

Elapsed Time		Initial	24 Hrs	44 Hrs	69 Hrs
Sample #	Clay Conc. (mg/l.)	Acidity in meq/l			
1	85	----	0.24	0.17	0.48
2	280	0.17	0.23	0.15	1.29
3	1390	0.54	0.17	0.15	2.00
4	6950	1.03	0.39	0.47	2.30
5	11,100	2.19	1.35	----	2.35
6	20,800	2.92	1.89	1.29	2.37
7	27,800	5.54	2.66	2.24	2.28

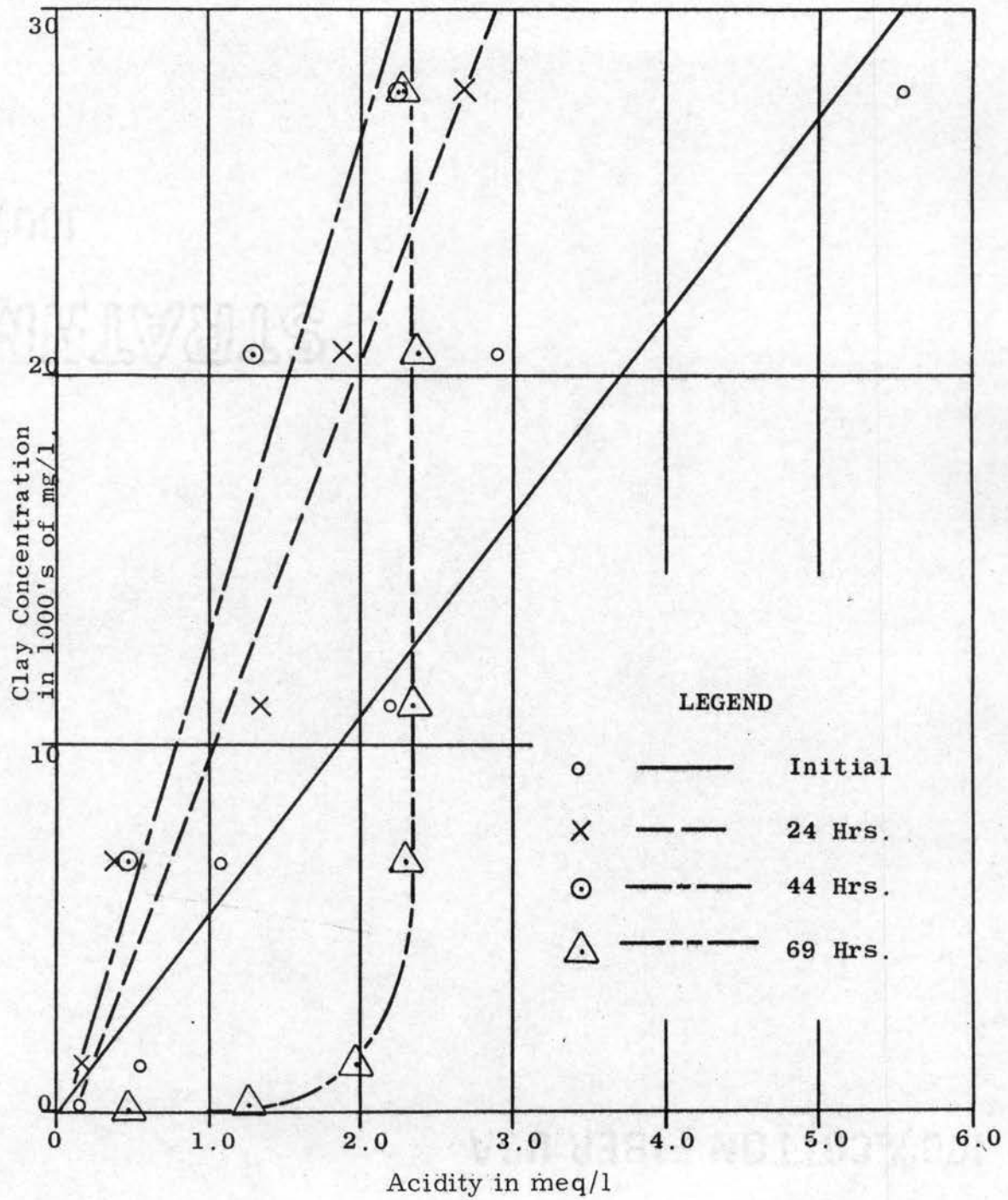


Fig. 3-3

ILLITE CLAY CONTROL CURVES

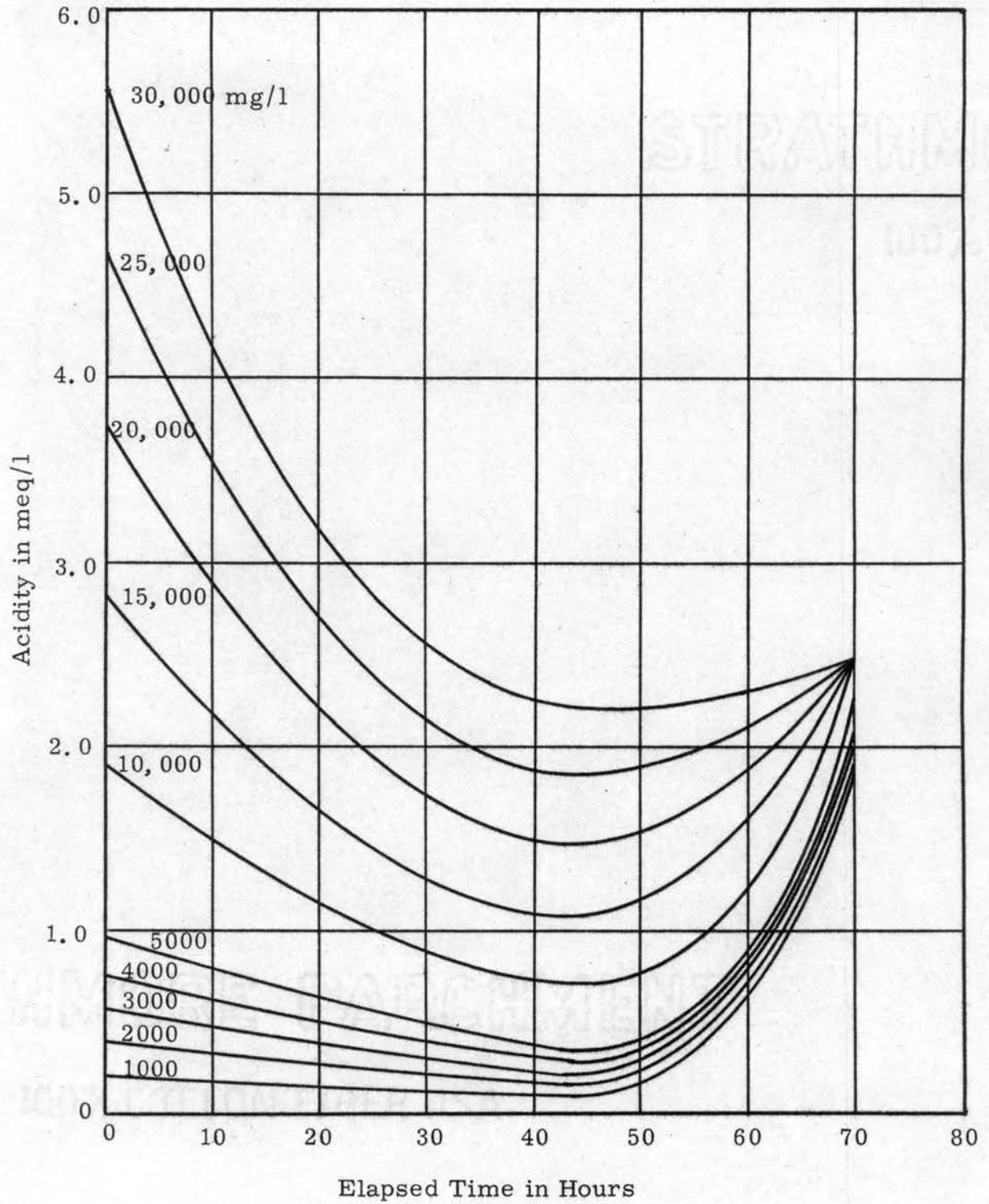


Fig. 3-4

Illite Clay Acidity Correction Curves

TABLE 3-9

CORRECTED AND UNCORRECTED EXPERIMENTAL SORPTION DATA FOR
ILLITE AND ACETIC ACID

Sample #	Clay Conc. (mg/l)	Experimental Data Acidity in meq/l							
		Uncorrected				Corrected			
Elapsed Time in Hours		Initial	6	24	48	Initial	6	24	48
1	1110	3.13	2.90	2.67	2.56	2.78	2.58	2.34	2.36
2	1110	4.64	4.26	4.10	3.87	4.29	3.94	3.87	3.67
3	1110	10.10	9.80	9.70	9.30	9.65	9.48	9.47	9.10
4	1110	14.40	14.20	13.80	13.50	14.05	13.88	13.57	13.30
5	1110	20.00	19.80	19.60	18.90	19.65	19.48	19.37	18.70

TABLE 3-10

ISOTHERM DATA FOR ACETIC ACID AND
ILLITE AT 48 HRS.

Sample #	Clay Conc. (mg/l)	(y) Acid Sorbed in meq/l	(C) Acid in soln. in meq/l	(y/m x 10 ³) Acid sorbed/clay Conc. (mg/l) in mg/meq.
1	1110	0.42	2.36	0.378
2	1110	0.62	3.67	0.558
3	1110	0.45	9.10	0.405
4	1110	0.75	13.30	0.675
5	1110	0.95	18.70	0.855

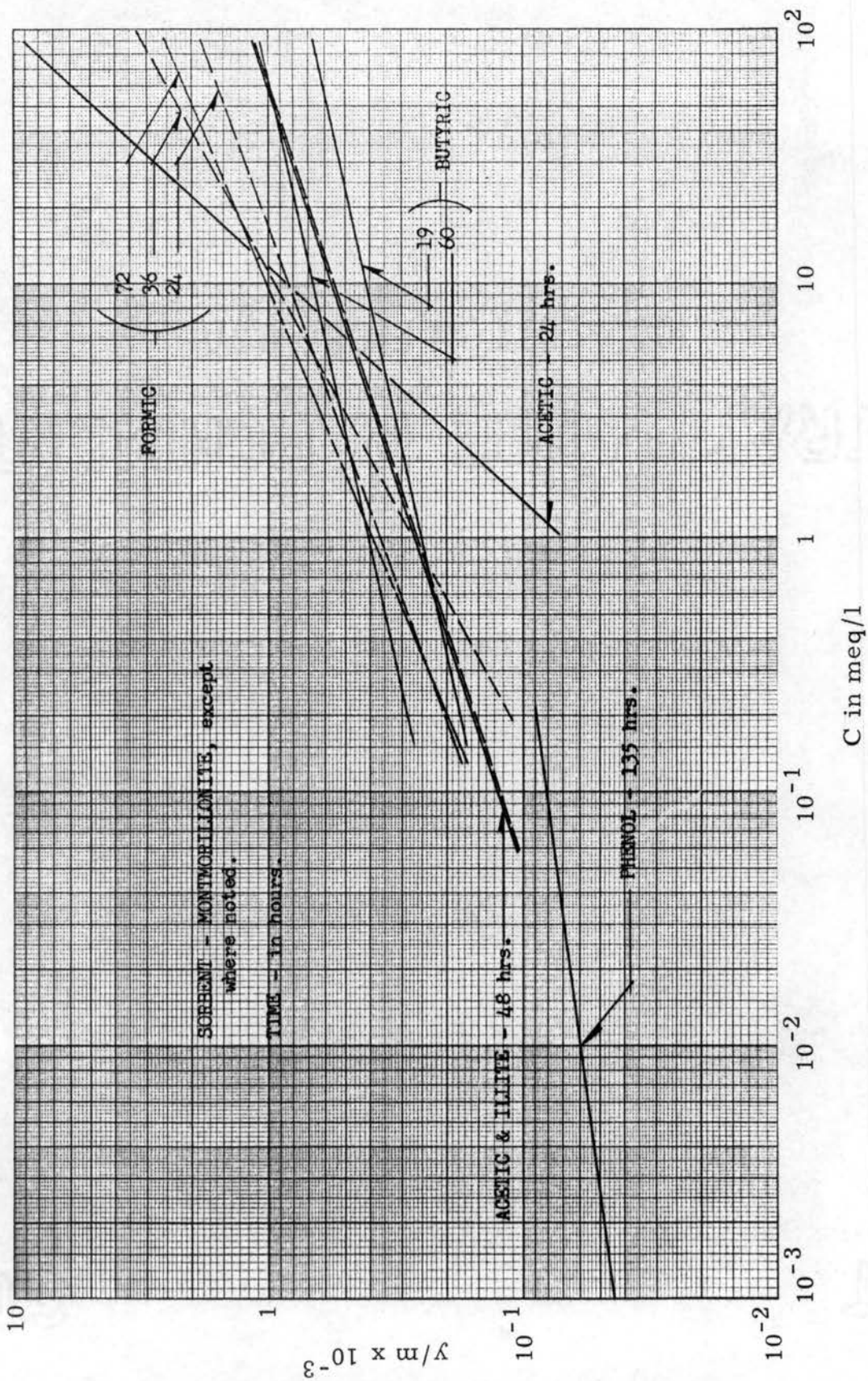


Fig. 3-5
ISOTHERMS

greater extent by montmorillonite than were the other acids. In lower concentrations, below 7 meq/l, illite sorbs acetic acid to a greater extent than does montmorillonite. The extent of acetic acid sorption by montmorillonite was less than that for the other acids studied below a concentration of 1.7 meq/l of acid remaining in solution.

The coefficients for the isotherm equations, obtained from the isotherms in Figure 3-5, are tabulated in Table 3-11. These coefficients are for the general form of the Freundlich isotherm, see section 1-5. Considering the n values from Table 3-11, which are indicative of the efficiency of a sorbent as stated in section 1-5, it can be seen that the order of effectiveness of the sorbents studied with respect to the acids is, mont-acetic, mont-formic, illite-acetic, mont-butyric, mont-phenol. The relative displacement of the isotherms occurs in this same order above an acid concentration of 13 meq/l.

3-2 Acetic Acid and Various Sorbents

The purpose of this set of experiments was to determine the variation in the percent sorption of acetic acid by illite, kaolinite, halloysite and activated carbon with respect to variations in sorbent concentration. Experiments were performed in a closed system at ambient temperature, 26° C., while holding the initial acetic acid concentration constant and varying the sorbent concentration.

Experimental results are presented, in each subsection, as percent sorption of acetic acid vs. sorbent concentration curves, at various elapsed times. Discussion of these curves appears at the end of each subsection. Experimental results were also presented, in subsection E., as percent sorption of acetic acid vs. C/A ratio, sorbent concentration over initial acetic acid concentration, curves, (see Figure 3-10).

TABLE 3 - 11

FREUNDLICH ISOTHERM COEFFICIENTS
 $(Y/M = k C^n)$

	Elapsed Time in Hrs.	$k \times 10^4$	n
Montmorillonite-Formic	24	3.67	0.356
	36	2.70	0.551
	72	3.74	0.421
-Acetic	24	0.70	1.100
-Butyric	19	2.50	0.223
	60	4.12	0.212
-Phenol	135	1.08	0.132
Illite - - - - - Acetic	48	2.70	0.318

Comparisons of the sorption capacities of illite, kaolinite, halloysite and activated carbon for acetic acid were made from the above curves and are discussed at the end of subsection E.

A. Acetic Acid and Illite

In this experiment the initial concentration of acetic acid was held constant at 23.12 meq/l, with the concentration of illite varied from 2220 mg/l to 55,500 mg/l. Experimental results were corrected for illite clay acidity, illite and distilled water, from the curves in Figure 3-4. Clay acidity correction data for the sample containing illite in a concentration of 55,500 mg/l, was obtained by a linear extrapolation of the illite concentration vs. clay acidity curves in Figure 3-3. The experimental sorption data, both corrected and uncorrected, for acetic sorption by illite, at 24 and 48 hours elapsed time, is tabulated in Table 3-12. From the corrected data in Table 3-12, values for the present sorption of acetic acid, at 24 and 48 hours elapsed time, were developed, prepared and are tabulated, with respect to corresponding illite concentrations, in Table 3-13. The present sorption data, from Table 3-13, was plotted against corresponding illite concentrations to yield, 24 and 48 hour, percent sorption vs. sorbent concentration curves, shown in Figure 3-6.

The curves, in Figure 3-6, indicate that an illite concentration greater than 20,000 mg/l, begins to desorb acetic acid, after an elapsed time of 24 hours. The reason for the desorption of acetic acid by illite can be explained from an examination of the mechanisms by which the illite clay controls, illite and distilled water, change in acidity with respect to time, (see Figure 3-4). Illite, is composed of 7.88 percent "acid" water and no "basic" water. This fact indicates that the high

TABLE 3 - 12

CORRECTED AND UNCORRECTED SORPTION
DATA FOR ACETIC ACID
AND ILLITE
(Clay Varied)

Sample #	Illite Conc. (mg/l)	Uncorrected Data			* Corrected Data		
		ACIDITY IN MEQ/L. **					
Elapsed Time in Hours		Initial	24 hrs.	48 hrs.	Initial	24 hrs.	48 hrs.
		1	2220	23.12	23.42	22.29	23.12
2	5550	23.12	22.84	22.30	23.12	22.24	21.80
3	11,100	23.12	22.76	22.18	23.12	21.56	21.18
4	22,200	23.12	22.67	22.17	23.12	20.57	20.57
5	55,500	23.12	23.92	23.14	23.12	18.92	19.64

* Corrected for clay, illite and distilled water, acidity.

** The initial acidity of the acetic acid was determined before the addition of illite and, therefore, remain unchanged in the uncorrected data.

initial acidity of the illite clay controls is due to the immediate dispersion, into solution, of "acid" water. Once illite loses its "acid" water, it becomes basic with respect to the solution and acetic acid. During this period, the rate of sorption of acetic acid by illite is at its maximum value due to the columbic forces of attraction between illite and acetic acid. With passing time, there is a decrease in the acidity of the illite clay controls, that is caused by an exchange reaction taking place with respect to illite. Illite slowly exchanges potassium for the hydrogen ions in solution. ⁽¹¹⁾ With sufficient time, in a well mixed

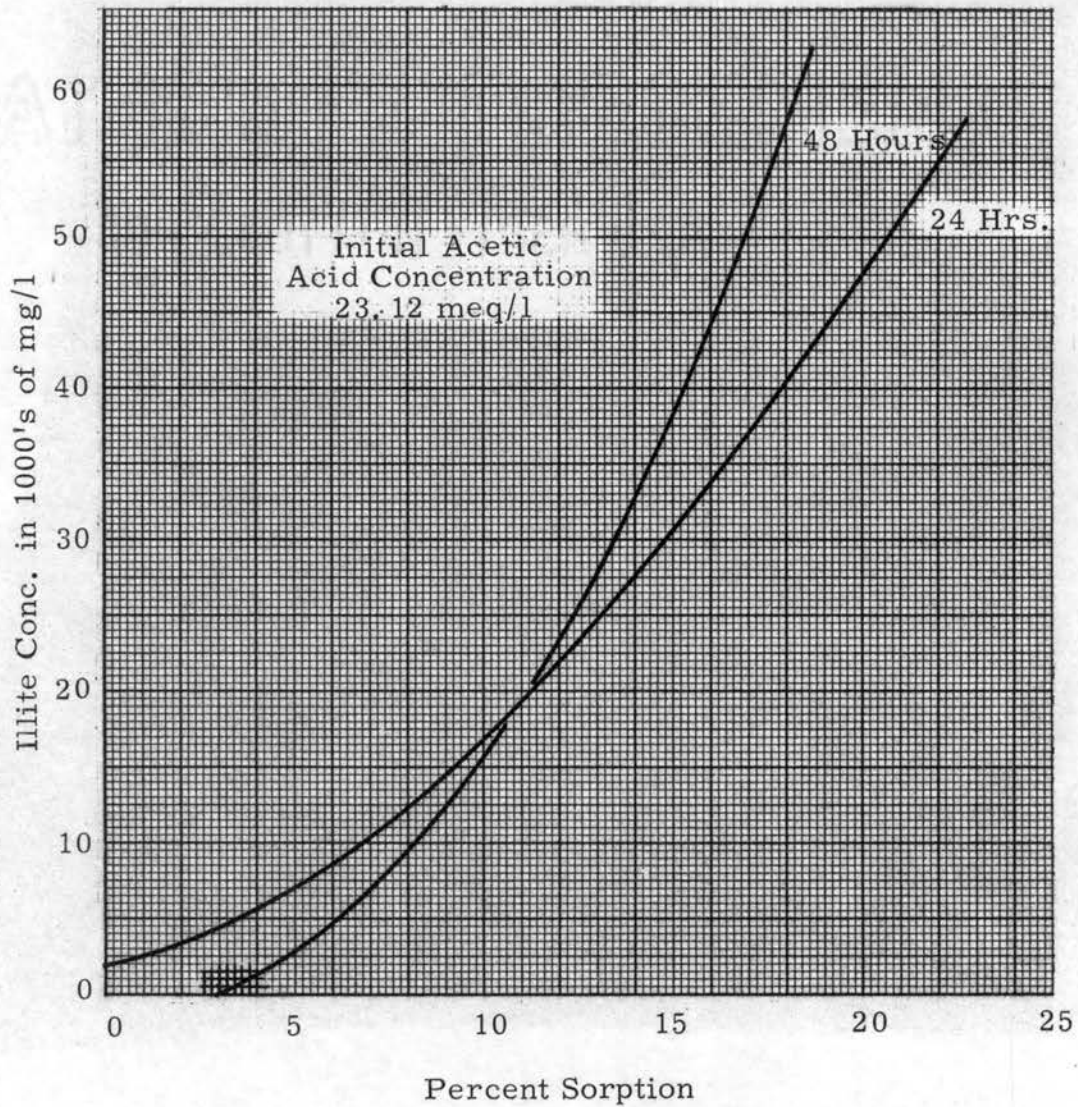


Fig. 3-6

Percentage Sorption vrs. Clay Concentration Curves at
24 and 48 Hours for Illite and Acetic Acid

TABLE 3 - 13

PERCENT SORPTION OF ACETIC ACID BY ILLITE

Sample #	Illite Conc. (mg/l)	C/A (mg/meq)	PERCENT SORPTION	
			24	48
Elapsed Time in hours			24	48
1	2220	96	0.00	4.75
2	5550	240	4.00	6.05
3	11,100	480	7.25	8.40
4	20,200	960	11.70	11.70
5	55,500	2400	22.20	17.70

* The C/A Ratio is the concentration of the sorbent divided by the concentration of acetic acid, initially in solution.

media, attrition between illite particles increases their charge deficiency and the illite clay controls once again become more acidic. This is evident in the illite concentration vs. clay acidity curves in Figure 3-4, between 40 and 50 hours. As the clay mineral, illite, becomes more acidic, approaching the acidity of acetic acid, the relatively weak sorption forces of illite⁽²⁹⁾ are overcome by the coulombic repulsion forces and acetic acid is desorbed.

At clay concentrations below 20,000 mg/l, illite continues to sorb acetic acid, with the difference, in percentage sorption of acetic acid, between the 24 and 48 hour curves of Figure 3-6, increasing with decreasing clay concentration. The above observation can be explained from a consideration of the sorption driving force per unit area of sorbent or, in other words, the sorption force concentration of the acetic acid.

As the clay concentration decreases, in a system containing a fixed total amount of acid, the amount of acid, in solution, per unit area of sorbent increases. Since the concentration of the sorbate is considered to be the sorption driving force, the sorption force per unit area of sorbent, or sorption force concentration then increases with decreasing clay concentration. It is therefore concluded, that as the sorption force concentration increases the amount of sorbate sorbed per unit area of sorbent also increases. This increased force concentration for the lower concentrations of illite, overcomes the previously mentioned coulombic repulsion forces and acetic acid continues to be sorbed by illite, even after 48 hours, as indicated by the curves in Figure 3-6.

In view of the above consideration, it was felt that multilayer sorption was occurring at the illite-acetic acid interface. A relative relation between illite concentration and depth of the sorbed acetic acid layer can be obtained by dividing the illite concentration by the corresponding, sorbed, acetic acid concentration. The relative values were prepared, from data taken from Figure 3-6, and are tabulated, along with corresponding illite concentrations and sorbed acetic acid concentrations, in Table 3-14, at 24 and 48 hours elapsed time.

From a consideration of Table 3-14, it can be seen that the thickness of the sorbed layer of acetic acid, generally decreases with increasing clay concentration. This is to be expected, since the sorption driving force concentration decreases with increasing clay concentration, thereby, causing the concentration of sorbate sorbed per unit area or sorbent to decrease with increasing clay concentration.

TABLE 3-14

RELATIVE THICKNESS OF SORBED ACETIC
ACID LAYER ON ILLITE

Illite Conc. (mg/l)	Acid Sorbed in meq/l (Acetic Acid)		Relative Layer Thickness x 10 ⁴	
	24	48	24	48
Elapsed Time in Hours				
2500	0.19	1.11	0.76	4.44
10,000	1.57	1.89	1.57	1.89
20,000	2.59	2.59	1.30	1.30
50,000	4.79	3.91	0.96	0.78

B. Acetic Acid and Kaolinite

This experiment was performed with the initial concentration of acetic acid fixed at 4.45 meq/l and the kaolinite concentration varied from 75 mg/l to 2230 mg/l. Pilot experiments, conducted to determine the change in acidity of kaolinite in distilled water with time, showed that the kaolinite produced no increased acidity or change in acidity with time different from pure distilled water.

The experimental sorption data for kaolinite and acetic acid, at 24, 36, and 48 hours elapsed mixing time, are listed in Table 3-15. The values listed in the above table were calculated using Equation 2-1. Graphic presentation of the above data, Figure 3-7, was prepared by plotting percent sorption against corresponding concentrations of kaolinite to yield the curves, for 24, 36, and 48 hours elapsed time.

Generally, the percent sorption of acetic acid by kaolinite curves indicate that above a clay concentration of 14,500 mg/l of kaolinite, after 48 hours elapsed time, sorption ceases. This relationship suggests a

TABLE 3-15

EXPERIMENTAL SORPTION AND PERCENT SORPTION
DATA FOR ACETIC ACID AND KAOLINITE

Sample #	Kaolinite Conc. (mg/l)	Experimental Data (Acidity in meq/l)				C/A (mg/meq)	Percent Sorption Data		
		Initial	24	36	48		24	36	48
1	75	4.45	4.21	4.36	3.66	17	5.39	2.02	17.75
2	140	4.45	4.12	4.15	3.54	31	7.42	6.74	20.45
3	285	4.45	4.28	3.78	3.24	64	3.82	15.06	22.20
4	565	4.45	4.30	3.59	3.46	127	3.37	19.33	22.25
5	1125	4.45	4.39	3.57	3.40	253	1.35	19.78	23.60
6	2230	4.45	4.17	3.80	3.42	501	6.29	14.61	23.14

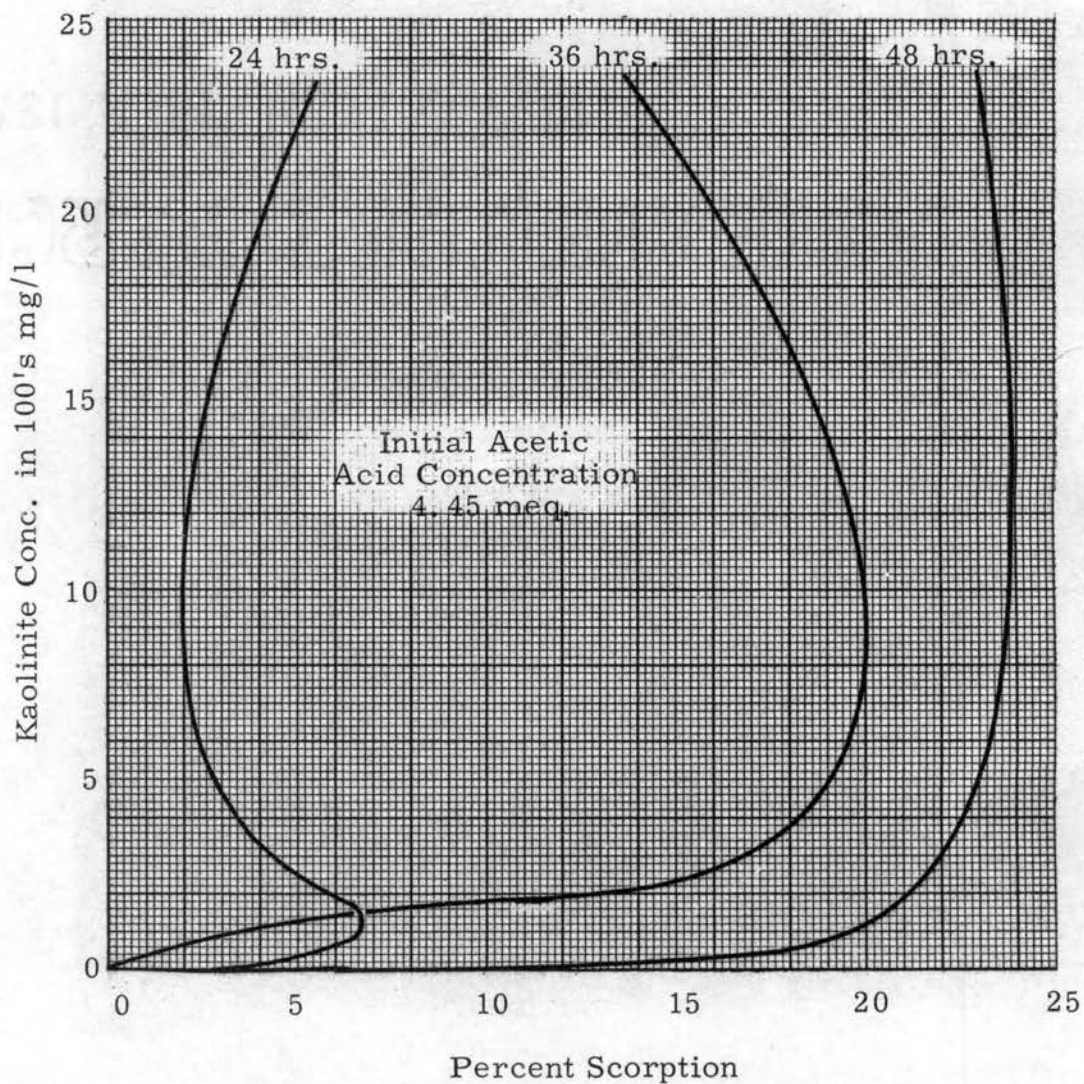


Fig. 3-7

Percentage Sorption vrs. Clay Concentration Curves at
24, 36, and 48 Hours for Kaolinite and Acetic Acid

threshold sorbent concentration for the sorption force concentration, sorbate concentration per unit area of sorbent. With an increasing sorbent concentration, the sorption force concentration decreases, in a system in which the total concentration or sorbate remains constant, as explained in the discussion of the results of experiment 3-2A. With increasing concentration of kaolinite, a threshold value for the sorption force concentration of acetic acid is reached, below this value the sorption force concentration is not great enough to sustain additional sorption.

In Section 1-4, it was stated, that when a sorbent was saturated with sorbate, an additional amount of sorbate added to the system would not initiate any further sorption. It can similarly be considered, that a sorbate becomes saturated with sorbent, when the addition of more sorbent will initiate no further sorption. In view of the above consideration, it can be said, that 4.45 meq/l of acetic acid becomes saturated by a kaolinite concentration of 14,500 mg/l.

The shape of the 24 and 36 hour percent sorption vs. kaolinite concentration curves, shown in Figure 3-7, reflects the rate of acetic acid sorption by kaolinite. These curves show decreasing acid concentration with increasing kaolinite concentration. An increasing clay concentration is associated with a decreasing sorption force concentration, and it can, therefore, be considered, that the rate of sorption of acetic acid by kaolinite is proportional to the sorption force concentration. As indicated by the 48 hour curve, the higher kaolinite concentrations begin to exceed the lower concentrations, in acetic acid sorption because the lower concentrations of kaolinite, due to their faster sorption rate, are approaching an equilibrium with the acetic acid. The equilibrium value

associated with the 48 hour curve can be approximated by a tangent to this line.

C. Acetic Acid and Halloysite

In this experiment the clay concentration was varied from 555 mg/l to 11, 100 mg/l of halloysite while the initial concentration of the acetic acid was held to approximately 21 meq/l. Pilot experiments, used to determine the acidity of halloysite in distilled water, showed that halloysite like kaolinite does not produce measurable changes in acidity with time.

The experimental sorption data for halloysite and acetic acid, mixed for 24, and 48 hours are tabulated in Table 3-16. Values for percent sorption of acetic acid by halloysite, at 24 and 48 hours elapsed time, were prepared, from the experimental data shown in Table 3-16. Data for the percent sorption of acetic acid by halloysite was plotted against corresponding concentrations of halloysite to yield the curves, for 24 and 48 hours elapsed time, shown in Figure 3-8.

TABLE 3-16

EXPERIMENTAL SORPTION AND PERCENT SORPTION DATA FOR ACETIC ACID AND HALLOYSITE

Sample #	Halloysite Conc. (mg/l)	Experimental Data (meq/l)			C/A (mg/meq)	Percent Sorption Data	
		Initial	24	48		24	48
1	555	21.9	19.6	19.1	25	10.5	12.8
2	1110	22.4	20.3	19.5	50	9.4	12.9
3	2220	20.4	19.6	17.2	109	3.9	15.6
4	5550	20.2	19.3	18.3	275	4.5	17.6
5	11, 100	20.4	19.9	16.8	544	2.5	17.6

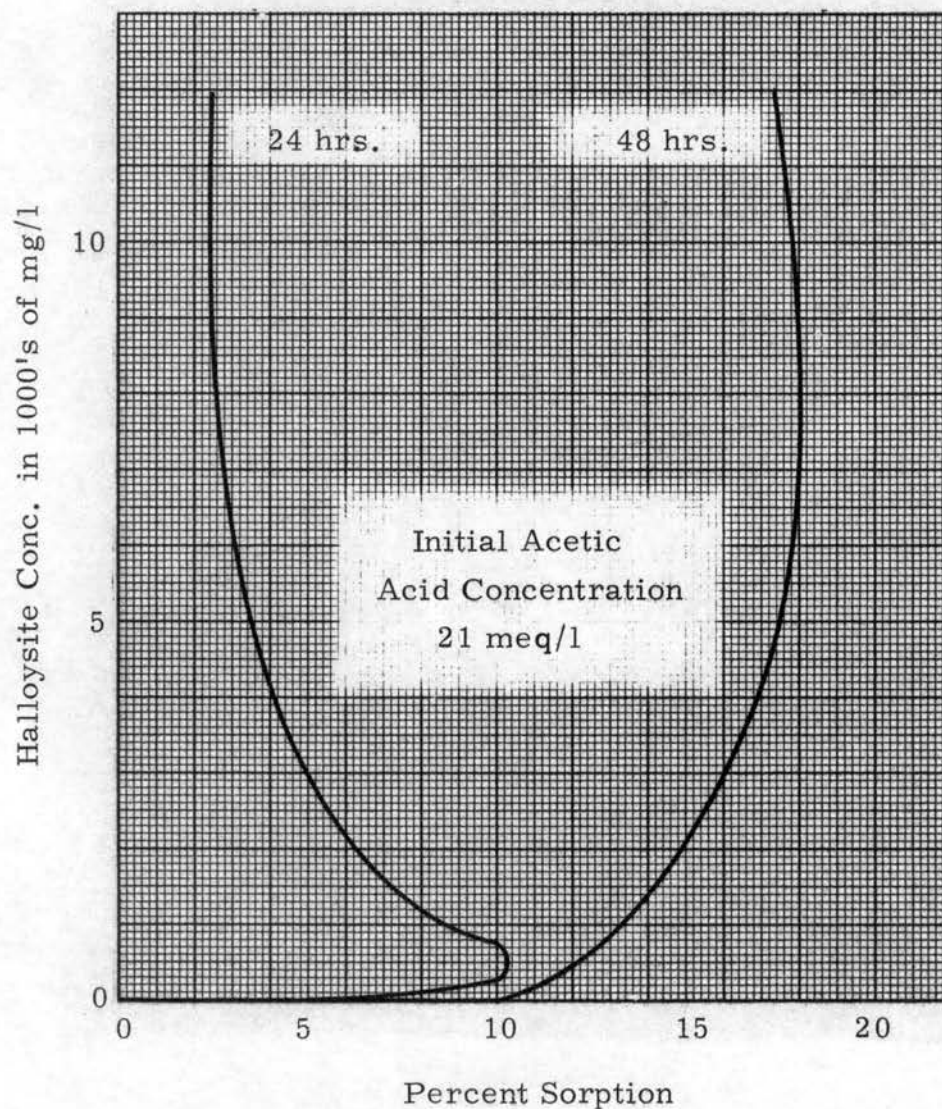


Fig. 3-8

Percentage Sorption vs. Clay Concentration Curves at
24 and 48 Hours for Halloysite and Acetic Acid

Inspection of the clay concentration vs. percent sorption curves, Figures 3-7 and 3-8, shows a similarity in the characteristics of acetic acid sorption by kaolinite and halloysite. The general shape of the 24 hour, kaolinite and halloysite, curves are similar. At 48 hours elapsed time the higher concentrations of halloysite begin to exceed the lower concentrations in acetic acid sorption, as was the case with kaolinite. Acetic acid, in a concentration of approx. 21 meq/l, becomes saturated with halloysite when the halloysite concentration exceeds 9000 mg/l, as determined by the point of tangency to the 48 hour halloysite curve from a vertical tangent.

The two clay minerals, halloysite and kaolinite, do not possess the same sorption mechanisms in that halloysite may sorb materials between its unit layers whereas kaolinite may not. They do, however, possess the same sorption characteristics for acetic acid, suggesting that sorption of acetic acid by halloysite is a surface phenoma because this surface phenoma is the only way in which materials are sorbed by kaolinite.

D. Acetic Acid and Activated Carbon

The concentration of the acetic acid, in this experiment was held constant at 19.86 meq/l while the activated carbon concentration was varied from 55 mg/l to 11,100 mg/l. Activated carbon shows no acidic or basic hydrolysis in distilled water.

The experimental sorption data for acetic acid and activated carbon, at 6 and 24 hours elapsed time, is tabulated in Table 3-17. Percentage sorption values for acetic acid, at 6 and 24 hours, were prepared from the experimental data and are tabulated in Table 3-17. Percent sorption data was plotted against corresponding concentrations of

activated carbon to yield the curves, for 6 and 24 hours elapsed time, in Figure 3-9.

TABLE 3-17

EXPERIMENTAL SORPTION AND PERCENT SORPTION
DATA FOR ACETIC ACID AND ACTIVATED CARBON

Sample #	Act. Carbon Conc. (mg/l)	Experimental Data (Acidity in meq/l)			C/A (mg/meq)	Percent Sorption Data	
		Initial	6	24		6	24
1	55	19.86	19.75	19.31	3	0.56	2.77
2	220	19.86	19.53	19.10	11	1.66	3.83
3	1110	19.86	18.66	18.34	56	6.05	7.65
4	5550	19.86	16.06	15.30	280	19.15	22.96
5	11,100	19.86	11.72	11.50	559	41.00	42.09

The percent sorption of acetic acid vs. activated carbon concentration curves, in Figure 3-9, show that the sorption of acetic acid by activated carbon is directly proportional to the carbon concentration. Activated carbon sorbs most of the acetic acid during the first 6 hours, as indicated by the small variation between the 6 and 24 hour curves in Figure 3-9. Sorption of acetic acid by activated carbon, as indicated by the curves in Figure 3-9, does not involve a threshold value of the sorption force concentration. There is no indication that acetic acid becomes saturated by the carbon.

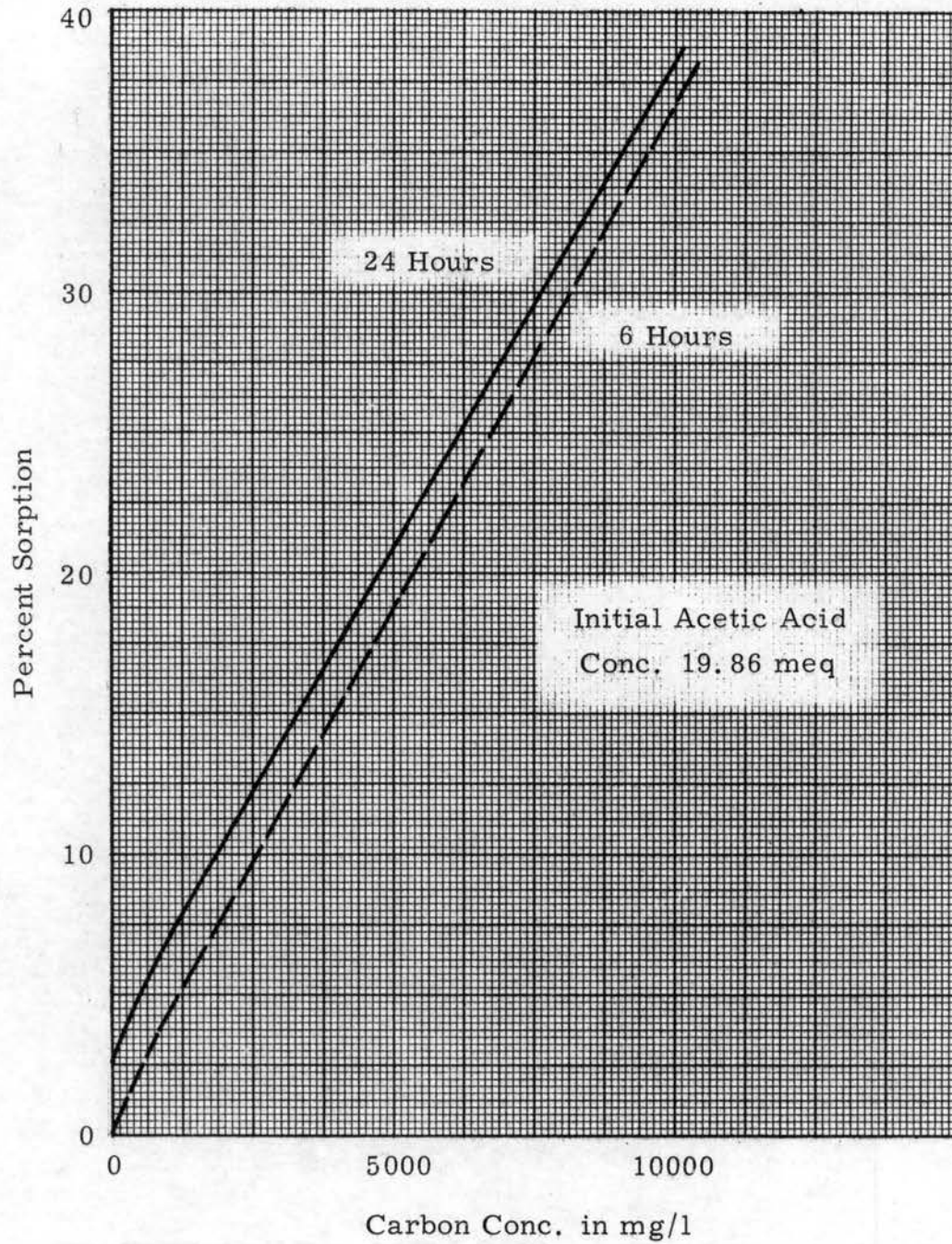


Fig. 3-9

Percent Sorption vs. Carbon Conc. Curves for Activated Carbon and Acetic Acid at 6 and 24 hours

E. Comparison of Acetic Acid Sorption by Various Sorbents

Comparison of the rate and amounts of acetic acid sorbed by various sorbents provides a relative index of sorption efficiency and direct consideration of sorption reactions. The results used for the above comparison were taken from the percent sorption data, in Tables 3-13, 15, 16, 17, using the 48 hour data for the clay minerals and 24 hour data for activated carbon. These results were plotted against their corresponding C/A ratio, sorbent concentration over initial concentration of acetic acid, to yield the curves in figure 3-10.

A comparison between the sorption capacities of illite, kaolinite, halloysite and activated carbon for acetic acid is shown in Figure 3-10. Inspection of Fig. 3-10 shows the variation in acetic acid sorption by the clay minerals kaolinite, halloysite, illite. Kaolinites and halloysite-acetic acid sorption capacities are, respectively, 3 to 4 and 2 to 3 times greater than that of illite. With an increasing C/A ratio, the acetic acid sorption capacities of illite and halloysite approach that of kaolinite. This is due to the acetic acid becoming saturated in kaolinite at lower C/A values than for either illite or halloysite, as shown by the flatening out of the kaolinite curve at lower C/A values. The curves for the clay minerals are similar in shape, with the rate of percentage sorption with respect to C/A being initially high, thereafter decreasing with an increasing C/A. In the case of kaolinite and halloysite, the curves reach a maximum percentage sorption value, thereafter, decreasing in percentage sorption with an increasing C/A ratio. A consideration of the maximums for the kaolinite and halloysite curves, indicates that, acetic acid becomes saturated with kaolinite at a C/A value of approximately 325, with halloysite, 425. With illite there is no indication of acetic acid becoming

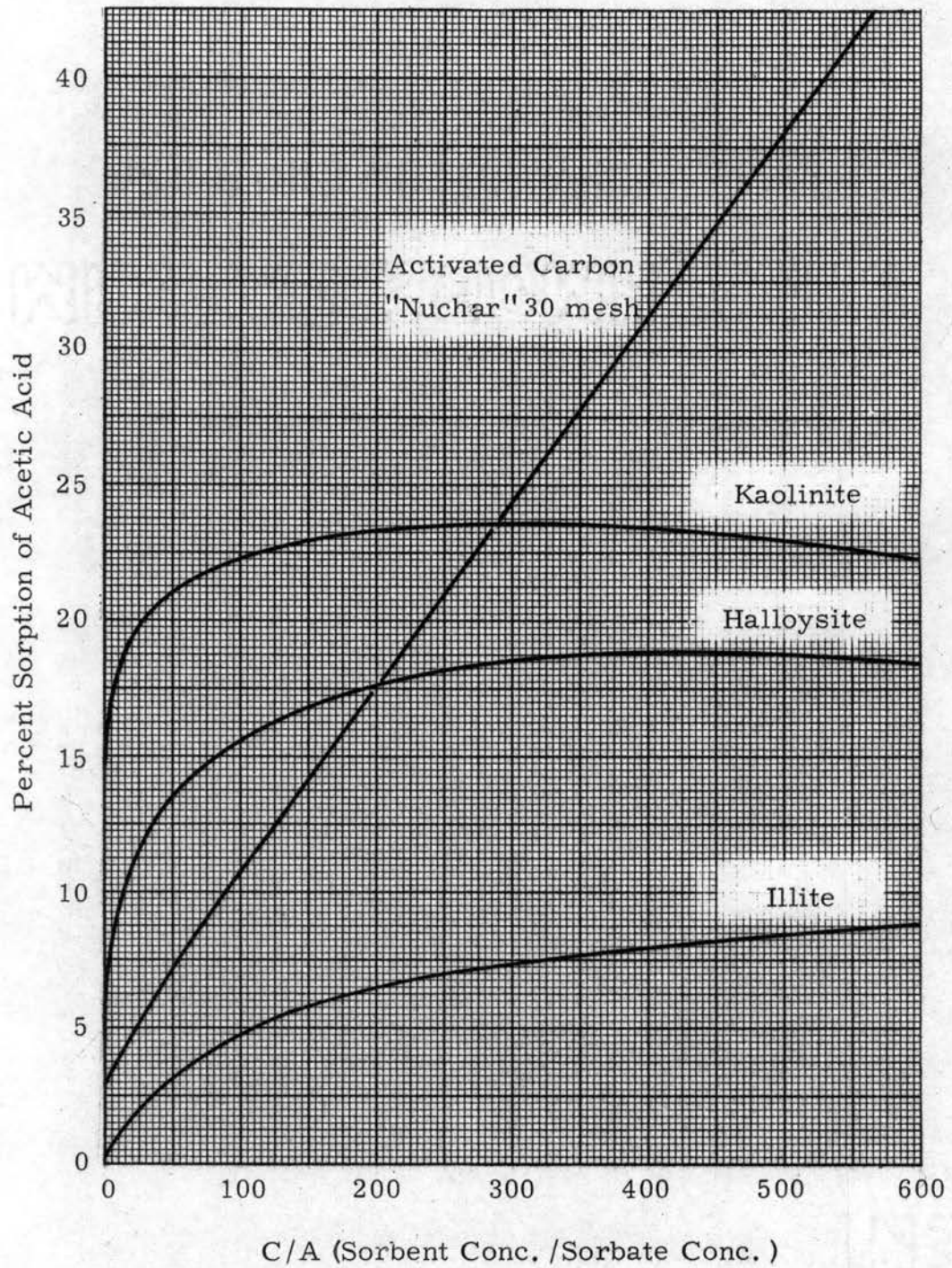


Fig. 3-10

Percent Sorption of HAc vs. C/A Curves for Illite, Kaolinite and Halloysite at 48 Hrs and Activated Carbon at 24 Hrs.

saturated for C/A values from zero to 2400, as shown by the data in Table 3-13.

Above a C/A ratio of 282, activated carbon exhibits a greater sorption capacity for acetic acid than does illite, kaolinite or halloysite, as indicated by the curves in Figure 3-10. Sorption of acetic acid by activated carbon is directly proportional to the carbons concentration or C/A ratio. Below a C/A ratio of 282, activated carbons sorption capacity is less than kaolinites, below 200, it is less than halloysites, it is, however, never less than the acetic acid sorption capacity of illite.

3-3 Comparison Experiments

Comparison experiments were used to explore the effects on sorption by varying temperature, sorbates and sorbents. The sorbents studied were the aliphatic carboxylic acids, formic, acetic, propanoic, butyric, iso-butyric and valeric, in an initial concentration of approximately 3.5 meq/l. Clay minerals, montmorillonite and kaolinite were studied, in conjunction with the above acids, in a concentration of 1110 mg/l. All experiments used an open container mixing vessel and six place stirrer. An evaluation of temperature effects on sorption was obtained from the experimental results of similar experiments performed at temperatures of 12, 22 and 33° C. Temperature of the solution was controlled by a constant temperature water bath.

Control experiments were conducted to correct the experiments for changes in acidity due to clay acidity and acid volatilization. Experiments, involving montmorillonite as the sorbent, were corrected for clay, montmorillonite and distilled water, acidity from the data in Table 3-1. The clay acidity correction values, from Table 3-1, were multiplied by 1110/1220 to adjust them for a montmorillonite concentration of

1110 mg/l, as the data in Table 3-1 was for montmorillonite in a concentration of 1220 mg/l. The clay mineral kaolinite showed no initial acidity and remained neutral with respect to time. Controls for the organic acids studied exhibited a change in acidity with respect to time and the experimental results from these controls, for temperatures of 12, 22, and 33° C., are tabulated in Table 3-18. Values for the percentage depletion in the acid controls, at various times, were prepared from the data in Table 3-18 and are tabulated, with respect to elapsed time, in Table 3-19.

TABLE 3-18

CARBOXYLIC ACID CONTROL DATA

Acid	Acidity in meq/l									
	12° C.			33° C.			22° C.			
Temperature										
Elapsed Time In Hours	Initial	24	48	Initial	24	Initial	24	48	144	
Formic	2.50	2.15	2.03	2.15	1.93	2.54	1.91	1.85	1.32	
Acetic	2.72	2.46	2.35	1.95	1.75	2.96	2.86	2.75	2.30	
Proponic	2.19	1.91	1.79	1.93	1.72	3.13	2.55	2.42	2.29	
Butyric	2.29	2.21	2.11	1.92	1.81	2.68	2.53	2.42	2.05	
Iso-Butyric	2.45	2.19	2.06	1.80	1.82	2.64	2.38	2.23	1.83	
Valeric	2.29	2.17	2.14	1.93	1.97	2.49	3.32	3.13	2.80	

TABLE 3-19

PERCENTAGE DEPLETION OF ACID
IN THE ACID CONTROLS

Acid	Percent Depletion of Acid					
	12° C.		22° C.			33° C.
Temperature						
Elapsed Time In Hours	24	48	24	48	144	24
Formic	14.0	18.8	24.8	27.2	48.0	10.2
Acetic	9.6	13.6	3.4	7.1	22.3	10.3
Propionic	12.8	18.3	18.5	22.7	26.8	10.9
Butyric	3.5	7.9	5.6	9.7	23.5	5.7
Iso-butyric	10.6	15.9	9.8	15.5	30.7	- 1.1
Valeric	5.2	6.6	4.9	10.3	19.8	- 2.1

The experimental results, for experiments using montmorillonite as the sorbent, were directly corrected for clay acidity by subtracting the clay acidity, montmorillonite adjusted to 1110 mg/l, from the experimental results of the corresponding elapsed time. Experimental results uncorrected for clay acidity were tabulated in Table 3-20 along with the corresponding elapsed time. Corrected experimental results are tabulated in Table 3-21. The corrected experimental results, from Table 3-20, were further corrected for acid loss through volatilization. This correction was made by using the acid control data in Table 3-19, through use of the method for acid control correction stated in Section 2-3, methods of analysis. A sample calculation of the above correction for acid volatilization appears in Appendix C. The results, in the form of percent sorption of acid, are listed along with their corresponding

TABLE 3-20

UNCORRECTED SORPTION DATA FOR THE CARBOXYLIC ACIDS
AND THE CLAY MINERALS KAOLINITE
AND MONTMORILLONITE

SORBENT	KAOLINITE			MONTMORILLONITE									
	22° C.			22° C.				12° C.		33° C.			
Temperature	22° C.			22° C.				12° C.		33° C.			
Elapsed Time	Initial	48	144	Initial	24	48	144	Initial	24	48	Initial	6	24
SORBATE	corrected as is (no clay acidity)			ACIDITY IN MEQ/L.									
FORMIC	3.37	1.85	1.25	3.50	2.64	ext(exp 3-1B)		4.24	3.59	3.55	3.80	3.52	2.80
ACETIC	4.45	3.40	3.15 ¹ *	3.78	3.04	2.78	2.30	4.85	4.49	4.34	3.49	3.29	2.92
PROPIONIC	3.22	2.68	2.00	3.06	2.76	2.54	1.92	3.76	3.62	3.63	3.39	3.25	2.52
BUTYRIC	2.99	2.34	1.68	corrected data in table 3-21				4.35	4.10	4.10	3.56	3.14	2.58
ISO-BUTYRIC	3.31	2.34	1.68	2.92	2.62	2.36	1.91	4.31	3.90	3.87	3.58	2.88	2.80
VALERIC	3.57	3.12	2.52	3.29	3.00	2.66	2.37	4.27	3.78	3.61	3.88	3.19	2.92

* estimated.

1 - data at the corresponding clay concentration taken from Table 3-15.

2 - data taken from a curve prepared from the corrected data at the corresponding clay concentration in Table 3-5.

TABLE 3-21

SORPTION DATA CORRECTED FOR CLAY ACIDITY FOR THE CARBOXYLIC
ACIDS AND MONTMORILLONITE

Temperature	12° C.			22° C.				33° C.		
Elapsed Time	Initial	24	48	Initial	24	48	144	Initial	6	24
SORBATE	ACIDITY IN MEQ/L.									
FORMIC	3.88	3.10	2.99	3.14	2.15	2.15	2.00	3.44	3.10	2.23
ACETIC	4.49	4.00	3.78	3.42	2.55	2.22	1.45	3.13	2.87	2.35
PROPIONIC	3.40	3.11	3.07	2.70	2.27	1.98	1.07	3.03	2.83	1.95
BUTYRIC	3.99	3.61	3.54	2.36	1.88	1.72	1.45	3.20	2.72	2.01
ISO-BUTYRIC	3.95	3.41	3.31	2.56	2.13	1.80	1.06	3.22	2.46	2.23
VALERIC	3.91	3.29	3.05	2.93	2.51	2.10	1.52	3.52	2.77	2.35

temperature and elapsed time, in Table 3-22. This percent sorption data for the carboxylic acids with respect to kaolinite and montmorillonite was plotted against the number of carbon atoms in the corresponding acid to yield, 1) the family of curves, percent sorption vs. number of carbon atoms, for different elapsed times, of kaolinite and montmorillonite at 22° C., Figure 3-11, 2) the family of curves, percent sorption vs. number of carbon atoms, of montmorillonite at the temperatures 12, 22 and 33° C. at 24 hours elapsed time, Figure 3-12.

Generally, the curves for the percent sorption vs. number of carbon atoms in the sorbate molecule, figure 3-11, show that the shape of the kaolinite 48 hour curve is similar to the 144 hour curve; whereas, for montmorillonite these respective curves are dissimilar in shape. This similarity and dissimilarity between the curves of kaolinite and montmorillonite suggest differences in the sorption mechanisms of the two clay minerals. An examination of the curves, in Figure 3-11, shows that the clay mineral montmorillonite desorbes formic and acetic acid after an elapsed time of 48 hours. Montmorillonite, however, continued to sorb, after 48 hours had elapsed. Since propionic and iso-but^orylic acid have the same maximum molecular dimension, 6.75 Å, the relatively large increase in their sorption by montmorillonite may be due to a geometric tunnel effect. This tunnel effect can be considered to be the inter-layer sorption of a molecule or ion of just the right size to react with regularly spaced unsatisfied lattice bonds on the inter-layer surface, see Section 2-4. This method of sorption is slow, as indicated by the sorption lag of propionic and iso-but^orylic acid, shown in Figure 3-11. One explanation of this slow reaction rate is the acid molecules must orient themselves in an exact direction prior to the sorption

TABLE 3-22

PERCENT SORPTION OF CARBOXYLIC ACIDS BY KAOLINITE
AND MONTMORILLONITE

SORBENT	KAOLINITE		MONTMORILLONITE					
	22° C.		12° C.		22° C.		33° C.	
Temperature								
Elapsed Time	48	144	24	48	24	48	144	24
SORBATE	PERCENT SORPTION							
FORMIC	30.3	45.1	9.0	8.5	14.6	13.1	5.7	28.5
ACETIC	18.2	13.5	2.4	4.5	22.8	30.4	26.9	17.3
PROPIONIC	- 2.2	21.1	- 3.2	- 6.8	0.4	10.0	49.6	28.7
BUTYRIC	14.0	31.4	6.3	4.3	15.7	19.9	24.2	33.8
ISO-BUTYRIC	18.4	33.5	4.6	2.8	8.6	18.8	45.7	31.7
VALERIC	3.6	15.4	11.5	16.9	10.2	20.8	37.9	34.7

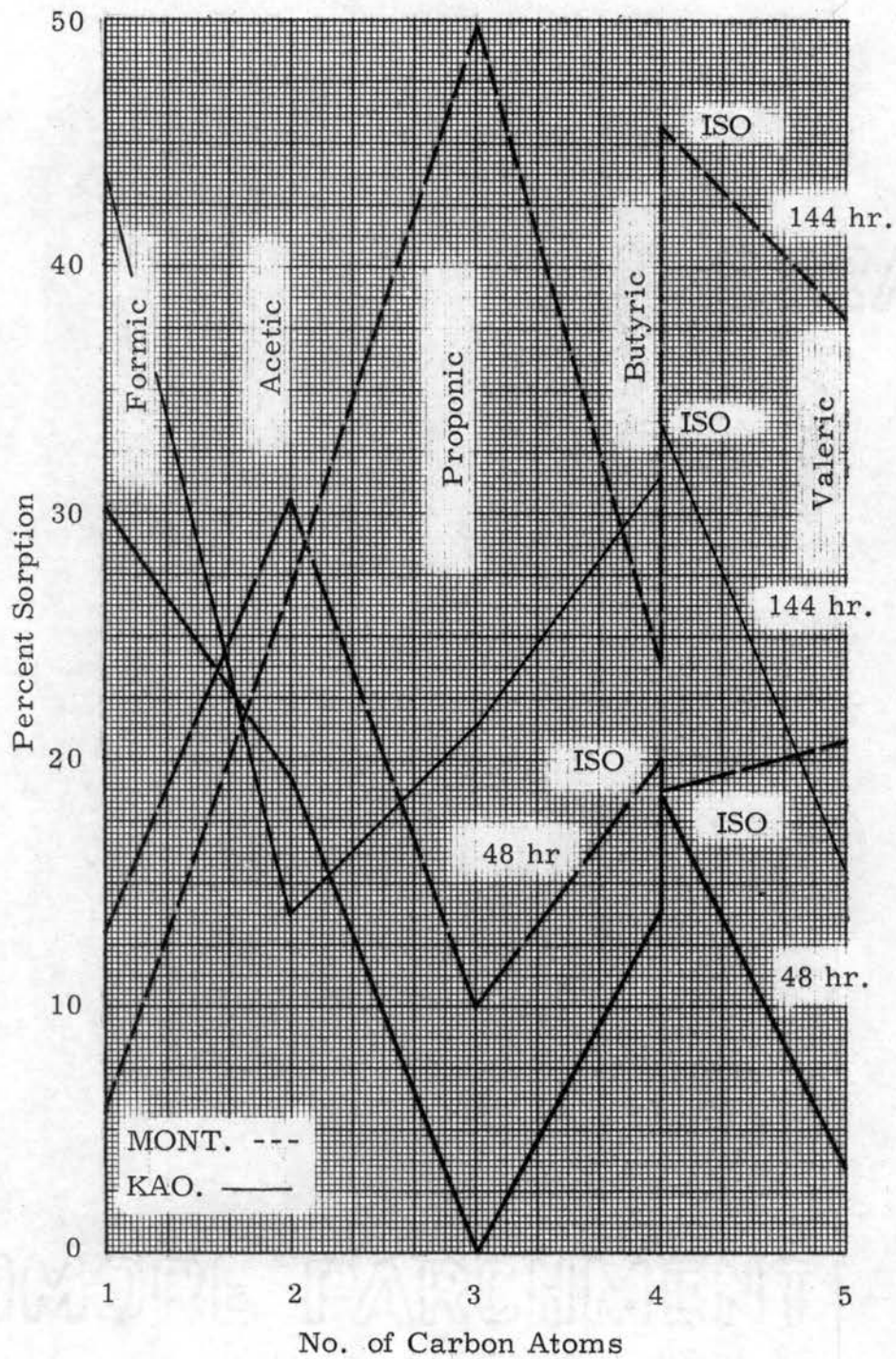


Fig. 3-11

Comparison of Kaolinite and Montmorillonite Sorption

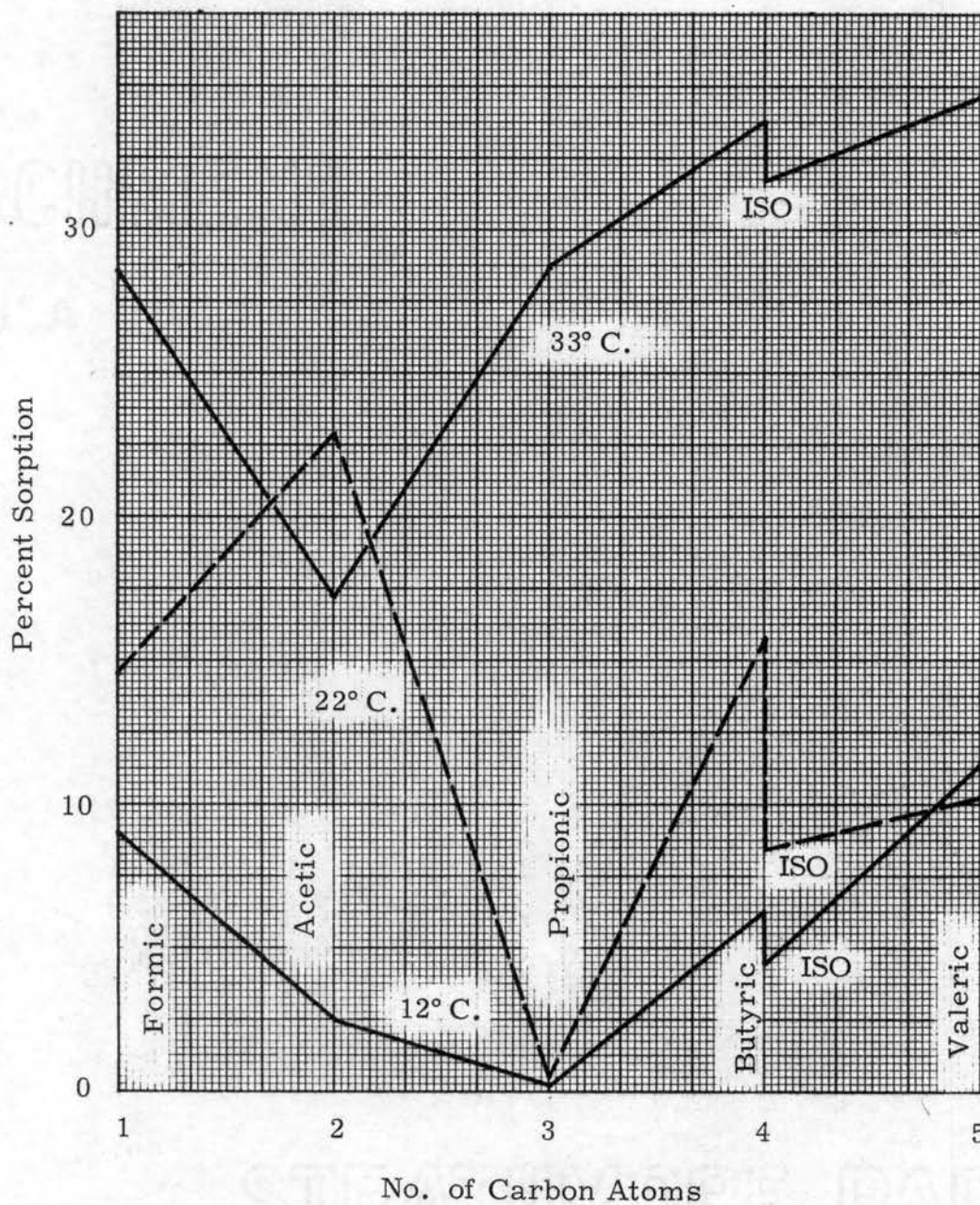


Fig. 3-12

Percent Sorption vs. # of Carbon Atoms for Montmorillonite
at 12, 22, and 33° C. at 24 Hours

reaction. An extension of this explanation indicated that orientation must precede sorption, hence it is the time limiting reaction. In addition, the orientation process is probably a random selection mechanism. Inspection of Figure 3-11 suggests that formic and acetic acid are sorbed on the surface of the montmorillonite clay particles and are therefore subject to desorption as the clay mineral montmorillonite becomes more acidic. (See section 3-2A).

Sorption of the carboxylic acids by the clay mineral kaolinite occurs only at the acid-kaolinite interface. This explains the similarity in the shape of kaolinites 48 and 144 hour curves, from Figure 3-11, in that all the acids are sorbed on the surface of kaolinite at generally the same rate, since the forces of sorption are the same. Montmorillonite, however, may sorb the carboxylic acids on its surface as well as between its unit layers, with the inter-layer sorption rate being slower than the surface sorption rate. Considering that acetic acid exists as a double molecule to a greater extent than do the other carboxylic acids, see section 2-2, it can generally be said that kaolinites sorption capacity is greater for the smaller and geometrically more compact acids. This can be explained from a consideration of the fact that the smaller the aliphatic carboxylic acid the greater is its dipole moment or the more polar is the molecule. It was stated in section 2-1 that polar molecules may be sorbed by the clay mineral due to the lack of symmetry of electron distribution within the molecule. This would allow the molecule to be sorbed from either end depending on the nature and charge of the sorbing surface.

An examination of the, 12° C., 22° C., and 33° C., curves, percent sorption vs. number of carbon atoms, from Figure 3-12, generally shows that an increase in temperature is associated with an increase in

the sorption rate of the carboxylic acids by the clay mineral montmorillonite. This can be explained from a consideration of the increased energy, due to a rise in temperature, within the aqueous clay-acid system.

The chemical potential or gibbs free energy per mole of material for a material is increased by a increase in temperature, as shown by an examination of equation 1-11.

$$\mu_2 = \mu_2^0 + RT \ln a_2 \quad (1-11)$$

The chemical potential of the solute, carboxylic acid in the system under study, was considered to be the sorption driving force in the derivation of the gibbs equation, see section 1-4. An increase in the chemical potential of the carboxylic acids should therefore increase the degree to which they are sorbed. Again from an inspection of the curves in Figure 3-12, it is obvious that only the carboxylic acids, formic and butyric, indicate sorption due to an increase in their chemical potentials. In addition these are the only acids that exhibit a somewhat linear increase in sorption with increasing temperature as would be the case if only the chemical potential of the sorbate had an effect on sorption. The non-linear sorption characteristics of the other carboxylic acids indicates that there is another temperature dependent mechanism through which sorption increases with increasing temperature.

The displacement of the sorbed water between the unit layers of the clay mineral montmorillonite by organic molecules is a sorption mechanism that is dependent upon temperature. An increase in temperature will decrease the viscosity of the sorbed water layer existing between montmorillonites unit layers. With increasing temperature it is, therefore, concluded that the acid molecules can more easily replace the less viscous central region of sorbed water molecules, existing between the

unit layers of montmorillonite, as their viscosity is decreased. Increased temperature not only increases the rate of sorption, but also increases montmorillonites sorption capacity, as indicated by an inspection of the 48 hour elapsed time columns for 12° C. and 22° C. in Table 3-22.

CHAPTER IV

SUMMARY AND CONCLUSIONS

4-1 Summary

An experimental evaluation of the sorption of one class of organics, the organic acids, by pure clay minerals is presented in this study. The experiments were limited to a simple bivalent system, one sorbate and one sorbent in a well-mixed aqueous system.

Several of the shorter chain carboxylic acids along with the enol, phenol, were studied due to their being contaminants in raw water supplies. Sorbents selected for the study were the pure clay minerals montmorillonite, illite, kaolinite and halloysite along with activated carbon, used as a comparison.

Results are presented graphically as Freundlich isotherms, percent sorption vs. clay concentration curves and percent sorption vs. number of carbon atoms in the sorbates molecule curves. Freundlich isotherms were obtained by conducting experiments in which the sorbate concentration was varied while the sorbent concentration remained fixed. Percent sorption vs. clay concentration curves were developed from experiments in which the sorbents concentration was varied while the initial concentration of sorbate remained fixed. Percent sorption vs. number of carbon atoms curves were obtained from experiments identical except for variations, one at a time, in temperature, sorbent and sorbate. Control experiments were used to correct for clay acidity

and loss of acid by volatilization.

4-2 Conclusions

Clay minerals have the ability to sorb organic acids in an aqueous system. The organic acids are selectively sorbed, the degree of which is governed by the magnitudes of the intensive and extensive properties of the system. The intensive properties studied in this thesis were type of sorbate and sorbent and temperature. Extensive properties studied were the concentrations of the sorbate and sorbent.

Montmorillonite was generally the most efficient sorbent followed by kaolinite, halloysite and illite in that order. The sorption of organic acids by montmorillonite was greatest for propionic acid, with extended contact time, being followed by iso-butyric, valeric, acetic, butyric, formic acid and the enol, phenol. With kaolinite, formic acid was sorbed to the largest degree followed by iso-butyric, butyric, propionic, valeric and acetic acid. This sequence of relative sorption by kaolinite generally remained valid for both 48 and 144 hours elapsed time. The sorption sequence for montmorillonite was, however, not the same at 48 and 144 hours elapsed time. This difference was explained on the basis of a so-called tunnel effect in which an acid has to hit the clay particle at just the right attitude to be sorbed. Since an acid molecule has no mobility of its own and therefore cannot align itself, the rate of sorption is then dependent upon the frequency with which an acid molecule having the proper alignment passes a sorption site. The acid molecule if in proper alignment will be sorbed at that site. This tunnel effect is believed to occur between the unit layers of a clay particle due to the fact that it is evident only with montmorillonite, which may sorb between its unit layers, and not with kaolinite, which may sorb only at its surface. This method

of sorption is slower than simple surface sorption as the frequency of molecules striking the surface of a clay particle is much greater than for the molecules passing between the clays unit layers.

The degree of sorption of a sorbate by a sorbent is dependent upon the concentration ratio between the sorbent and sorbate. It has been shown by percent sorption vs. clay over acid ratio data that when the C/A ratio increases, past a certain value, the percentage sorption remains constant. In the region of maximum percent sorption the acid or sorbate becomes saturated with sorbent and no further sorption will take place with an increased sorbent concentration. This leveling off of the percent sorption by increasing the clay concentration was explained on the basis of the sorption force concentration, sorbate concentration per unit area of surface offered by the sorbent, decreasing with increasing sorbent concentration, the total acid concentration in the system remaining fixed.

Temperature has a positive effect on sorption. This was shown by the experimental results and explained from a consideration of the increased system energy and the reduced viscosity of the sorbed interlayer water, both associated with an increased temperature. It cannot be explained on the basis of the system energy being referred to kinetic energy for the molecules of the sorbate because this would tend to decrease sorption, based on a consideration of sorption at a gas-solid interface. This increased system energy is, however, referred to an increase in the chemical potential of the sorbate, which decreases as the system tends toward equilibrium by driving the sorbate molecules toward a region of lower energy, that of an interface, see section 1-4. A decrease in the viscosity of the interlayer sorbed water would make it easier for the water molecules to be displaced by an organic material

of a higher sorption affinity.

Isotherms provide a method for presenting information which can then be transformed into a standard form equation. Isotherm equations were developed for the sorption of the carboxylic acids, formic, acetic, butyric and the enol, phenol, by montmorillonite and the sorption of acetic acid by illite. The Freundlich isotherm coefficients for the above sorbents and sorbates are listed in Table 3-11. The experimental data, for the isotherms, offered a good fit in the higher sorbate concentrations, above 50 meq/l. There was, however, a great deal of variation in the lower sorbate concentrations. Since the Freundlich isotherm is usually considered to be valid only for simple surface sorption, the variation in fit also indicates complex sorption reactions occurring in the lower sorbate concentrations. Plots of the isotherms when compared with each other offer a comparison between the degree and efficiency of sorption for the various sorbates and sorbents studied. From this comparison it was seen, that the sorption effectiveness, as indicated by the amount of sorption incurred by addition of an incremental amount of sorbate, for montmorillonite and acetic > montmorillonite and formic > illite and acetic > montmorillonite and butyric > montmorillonite and phenol.

4-3 Extension

The study of clay minerals role in the partitioning of organics in a natural water supply is a broad area of study, one in which much work remains to be done. This thesis is naive in its consideration of aqueous clay sorption in a natural environment. It does, however, offer a method through which further investigation may be conducted.

An immediate extension of this study would be the investigation of in situ clay sorption. This might be accomplished through an evaluation

of the partitioning by the clay minerals of one particular class of organics which are pollutants in a stream. This could be performed by measuring the concentration of the organics sorbed on the clays and in solution upstream from the organics source, then measuring the concentrations of the organics, at predetermined stations, sorbed and in solution. On conclusion of such an investigation a study of the in situ stability and biological availability of the sorbed materials should be initiated.

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APPENDIX A

SAMPLE CALCULATION

Determination of a Line of Best Fit by the
Method of Least Squares

Data from Table 3-1

Initial clay acidity

Statistical Data

x(meq.)	y(mg/l)	
5.54	27,800	$\Sigma x = 12.39$
2.92	20,800	$\Sigma y = 68,320$
2.19	11,100	$\Sigma y^2 = 1.379 \times 10^9$
1.03	6950	$\Sigma x^2 = 45.3955$
0.54	1390	$\Sigma xy = 247,013.7$
0.17	280	$N = 6$

$$y = C_0 + C_1 x$$

$$C_0 = \frac{\Sigma y - C_1 \Sigma x}{N} = 5347.4$$

$$C_1 = \frac{N \Sigma xy - \Sigma x \Sigma y}{N \Sigma x^2 - (\Sigma x)^2} = 344.28$$

$$y = 344 + 5350 x$$

This equation was used to plot the initial clay acidity line in Figure 3-3. The other straight lines were determined by the above procedure.

APPENDIX B

STATISTICAL ANALYSIS OF ISOTHERM DATA

To determine the straight line of best fit, for a Freundlich isotherm, on log-log paper, a modified method of least squares was used. This modification consisted of superimposing cartesian coordinates over the log-log coordinates. The isotherm data is plotted on the log-log paper with respect to the log-log axes. The isotherm values are then given coordinates from the cartesian system and used to determine the line of best fit by the least squares method, see Appendix A. This line of best fit is then plotted with respect to the cartesian coordinates on the log-log paper. The cartesian coordinates are then removed and the line becomes a Freundlich isotherm. A sample calculation of this method follows.

SAMPLE CALCULATION II

Determination of a Line of Best Fit by the Modified Method of Least Squares

The data for this sample calculation was taken from the 48 hour isotherm data in Table 3-4, for acetic acid and the clay mineral montmorillonite.

Data from Table 3-4		Data plotted on log-log paper then converted to cartesian coordinates.	
x(c)	y(y/m x 10 ³)	x'(C)	y'(y/m x 10 ³)
2.36	0.378	2.8	4.3
3.67	0.558	4.2	5.5
9.10	0.405	7.2	4.6
13.30	0.675	8.4	6.2
18.70	0.855	9.6	7.0

Statistical Data

$$N = 5$$

$$x = 32.2$$

$$y = 27.6$$

$$x^2 = 239.8$$

$$y^2 = 157.3$$

$$xy = 187.5$$

Using the equations from sample calculation I for C_0 and C_1 , the values for C_0 and C_1 are obtained.

$$C_0 = 3.48$$

$$C_1 = 0.318$$

Then the equation for the line to be plotted in cartesian coordinates is; $y = 3.48 + 0.318x$. Values satisfying this equation are plotted with respect to the cartesian grid that is superimposed over the log-log paper. The cartesian grid is removed and the line becomes a Freundlich isotherm.

APPENDIX C

Equation 2-2 was used to correct the experiments in Section 3-3 for acid loss due to volatilization. The sample calculation is for the sorption of Formic acid by montmorillonite at 22° C after 24 hours contact time, data from Table 3-21.

SAMPLE CALCULATION III

From Table 3-21

$$C_o = 3.14 \text{ meq/l}$$

$$C_{24} = 2.15 \text{ meq/l}$$

From Table 3-19

$$\% \text{ Depletion} = 24.8$$

$$\Theta_{24} \text{ Depletion} = .248$$

From Eqn. 2-2;

$$\Theta_{\text{sorb}}_{24} = \frac{3.14 - 2.15(1.248)}{3.14} = 0.146$$

Montmorillonite sorbed 14.6% of the formic acid at 22° C, in 24 hours.

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