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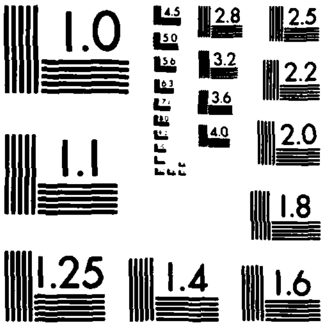

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Organic radical cations will dimerize when adsorbed to the surface of montmorillonite in colloidal solution. This dimerization is primarily the result of a concentration effect and the ability of organic probes to colonize or sequester on the clay particle surface or within its layers. The adsorption of organic cations to the clay surface is primarily a cation exchange process. The rate constant for cation exchange is 3.25×10^{6} L/equivalents^{-1}/sec^{-1}.

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REACTION OF PHOTOCHEMICALLY GENERATED ORGANIC CATIONS WITH COLLOIDAL CLAYS

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A Thesis
Submitted to the Graduate School
of the University of Notre Dame
in Partial Fulfillment of the Requirements
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Master of Science in Chemistry

REACTION OF PHOTOCHEMICALLY GENERATED ORGANIC CATIONS WITH COLLOIDAL CLAYS

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Master of Science in Chemistry

by

Louis Joseph Kovar, B.S.

Director

Department of Chemistry
Notre Dame, Indiana
May 1983

DEDICATION

I dedicate the work represented by this thesis to my wife, Maureen, and my son, John. They have supported me during long hours of studying and writing and always had an encouraging word when my research was not proceeding as expected. In addition, Maureen has followed me all over the world, endured long separations and six moves in the last eight years while I pursued my military career. For them, this thesis was truly a labor of love.

ACKNOWLEDGEMENTS

I gratefully acknowledge the assistance of my research director, Dr. J. Kerry Thomas. Dr. Thomas had no qualms about accepting me into his research group even though I had been out of school almost seven years and my ability to do scientific research was rusty if not nonexistant.

I further acknowledge the help and assistance of my co-workers Mr. James Wheeler, Mr. Joseph Kuczynski, Mr. Scott Becker, Dr. Ronald Dellaguardia, Dr. Shuichi Hashimoto and Dr. Brotoljub Milosavljovic. A special thanks is due to Jim Wheeler for his ability to program the Tektronix 4052A and therefore make life a little easier for everyone in the lab and Ron Dellaguardia who had been working with colloidal clays for a year prior to my arrival and had mastered many of the experimental techniques which are outlined in my thesis.

I thank LTC George Palladino, Ph.D., Professor of Chemistry at the United States Military Academy for encouraging me in the study of chemistry during my undergraduate days and selecting me to participate in the West Point Instructor program. I also acknowledge Chemical Branch, Department of the Army, MILPERCEN for selecting me to participate in a fully funded Master's Program and recommending me for a

teaching position at West Point.

I thank the faculty, staff and my fellow graduate students of the Chemistry Department, University of Notre Dame for making these last two years very enjoyable ones for my family and I.

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CHAPTER I

INTRODUCTION

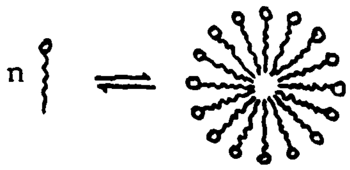
Forward

Photochemistry, the study of the interaction of light and other low energy radiation with matter,[37] is important to us in our daily lives. Vision, photosynthesis and other types of energy storage, as well as the formation of certain types of air pollutants are all the result of photochemistry.[14,23] Photochemists have undertaken the task of studying the intracacies of photochemical systems so that in the future certain aspects of these systems can be controlled preferentially. To this end photochemists have made great strides in the utilization of organized assemblies such as micelles, microemulsions, alcohol clusters, etc., to promote desirable features of photochemical reactions.[34] Most of these studies have been conducted with organized assemblies which are organic in nature [8,34] and it is appropriate at this time to extend these studies to inorganic systems [17,40] including clay colloids. [3,4]

The ability of clay minerals to catalyze thermal reactions is well documented.[32] This study will utilize this knowledge as well as current information on the photochemistry of anionic micelles, an organic analogue to clay colloids, to probe the photochemistry of organic molecules adsorbed on clays in colloidal solution.

The Nature and Chemistry of Micelles

As indicated previously, micelles, as well as clay colloids are specific examples of a more general entity in chemistry known as organized assembly. Thomas[34] has used the term "organized" to refer to a situation where some part of a system will aggregate or organize itself in deference to the bulk of the system, which is usually the solvent. Utilizing this definition then, micelles can be defined as aggregated structures formed by the interaction of surfactant molecules. A surfactant molecule (monomer) can be thought of as having a "tail" that is hydrophobic and a "head" that is hydrophilic. The hydrophobic part of a micelle monomer is usually a long-chain hydrocarbon and the hydrophilic part is some polar functionality. When the number of monomer units goes above a certain concentration known as the critical micelle concentration, CMC, they will group together (aggregate) forming micelles. In micelles the hydrophobic groups form a core separated from the solvent, usually water, by the hydrophilic head groups. A micelle is a dynamic structure in equilibrium with its monomer as depicted below:



(1)

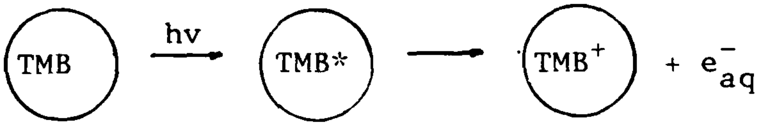
Micelles are generally considered to be small spheres or disks of 15-30Å radius, although some rod-like micelles have been reported. (See Thomas[34] for selected references.)

In anionic micelles such as those formed from sodium dodecyl sulfate, SDS, a significant portion of the head groups are ionized, the Na^+ counterions being in the region of the micelle surface or further into the aqueous bulk. These ions are generally considered to be in dynamic equilibrium with ions adsorbed at the micelle surface.

The ability of micelles to catalyze reactions has been known for some time and the last few years have seen detailed study of the effects of micellar systems on the rates of organic reactions.[7] Micellar systems are thought to catalyze reaction through two primary mechanisms. The first mechanism involves increasing local concentration of the reactants by effectively crowding them together through micelle, solute interaction. The second mechanism is the result of the suggestion that the ionic nature of the micellar surface influences the transition state of the reaction and can therefore hinder or promote the overall rate of the reaction. Since the proximity effect described in the first mechanism is not sufficient to explain catalytic efficiencies in micelles, the second mechanism is of much consequence.[7,8]

Types of reactions that are catalyzed by micelles include free-radical polymerization, energy transfer, electron transfer and photoionization, a special case of electron transfer in which the electron is transferred from the probe molecule to the solvent of the system.[34]

The photoionization of N,N,N',N', - Tetramethylbenzidine (TMB) has been studied in aqueous micellar solution.[1,8] SDS micelles have been shown to increase the yield of TMB monovalent cation (TMB^+) by efficiently separating the cationic species and the solvated electrons as depicted below:



(2)

Additionally micelles reduce the energy required for photoionization. TMB is photolyzed by one photon of 3451Å light the onset of photoionization being 3.0eV in micellar solution compared to 6.5eV in the gas phase.

THE NATURE AND CHEMISTRY OF CLAY MINERALS

Clay minerals are known to catalyze a wide range of chemical reactions including electron transfer, condensation and polymerization.[32] Of these, polymerization of certain organic compounds such as styrene has been of commercial importance in the past.[32,39] Currently clays are the focus of research since they are known to catalyze the decomposition of pollutants, such as pesticides, in the soil and are thought to have played a critical role in the generation of prebiotic materials.[39] Photochemists are interested in studying these reactions because new spectroscopic techniques and instrumentation allow them to learn much about the nature of the clay/organic complex. It is hoped that this knowledge will eventually permit the chemist to selectively and favorably influence reactions of interest.

Of the various types of categorized clay minerals, montmorillonite exhibits the most unique adsorption power for organic material and was the mineral of choice for this study.[35,36,39] Montmorillonite is described as a 2:1 expanding layer clay. This indicates that a planar sheet of aluminum atoms in octahedral configuration with oxygen shares some of these oxygen atoms with two sheets of silica atoms in tetrahedral configuration, one on each side (Fig. 1.) These three sheets make up a layer of montmorillonite clay.

Clay minerals do not consist solely of Al, Si, or O atoms in an organized array. Tetravalent silicon in the

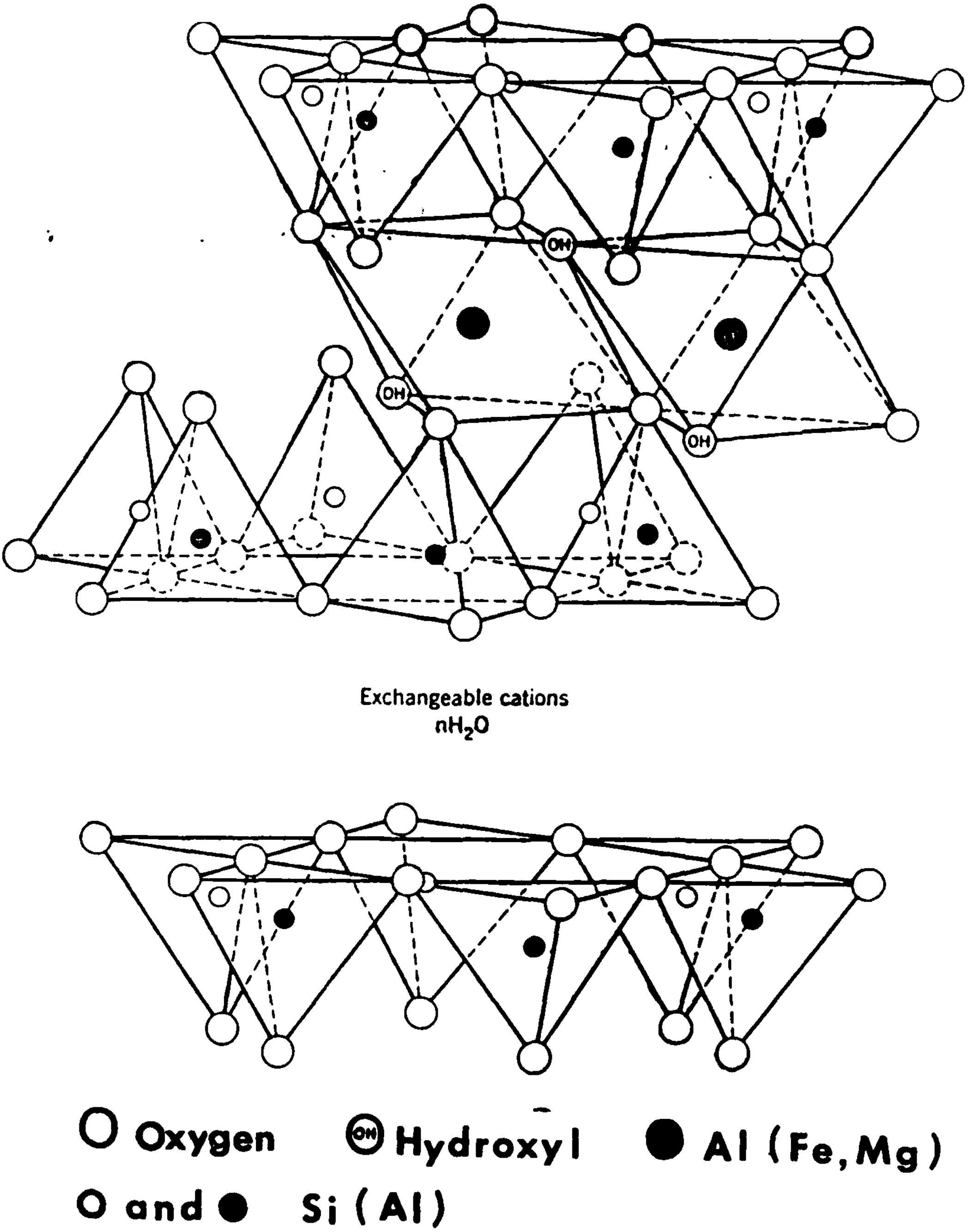


FIGURE 1. Diagrammatic Sketch of the Structure of Montmorillonite (from Grim[9]).

tetrahedral sheets may be replaced by trivalent species such as aluminum or ferric ion. Aluminum in the octahedral sheet may be replaced by manganous ion or ferrous ion. The small size of these atoms/ions permits them to take the place of the Si or Al atoms and is known as isomorphous substitution.[9,39] Isomorphous substitution results in a net negative charge on a clay particle due to the substitution of atoms in higher positive valence states by atoms of lower valence. The negative charge is balanced by the adsorption of cations such as Na^+ or Ca^{2+} on the particle (layer) surface. As in micelles these counterions exhibit kinetic action between the clay surface and the bulk phase and may be exchanged by other cations available in solution.[9,32,39] The ability of clay minerals to exchange counterions for other cations is known as the cation exchange capacity or CEC. The CEC is therefore a measure of the amount of substitution of the mineral and is usually expressed in milliequivalents per 100 grams of dry clay.[32]

Montmorillonite particles are constructed from stacks of layers, the number of layers determined by several factors including the chemical composition of the clay and the nature of the exchangeable cations.[9] Exchangeable cations are usually located on both sides of a layer in the stack and will therefore be located on both the surface of a montmorillonite particle and between its layers.

When dry montmorillonite is contacted with water, the water molecules penetrate between the layers causing the clay to swell. This process known as interlayer swelling can lead to at most a doubling of the volume of a dry clay.[39] When exposed to an excess amount of water, montmorillonite will continue to swell taking up an amount of water which is many times the volume of dry clay. This process is known as osmotic swelling.[39] In addition to water, organic compounds of an ionic or polar nature may be taken into the layers of montmorillonite particle.[26,27,29,31]

Chemical reactions of clay minerals include acid-base and oxidation-reduction reactions as well as many reactions which are catalyzed by acid-base or oxidation-reduction sites.[39] These sites, known as reactive sites, are generally considered to be of two primary types relating to their position on the clay particle.

When a layer of clay is broken during the formation of a particle the tetrahedral sheets and the octahedral sheets are disrupted and primary bonds are broken. These defects in the crystal structure of the clay leave Al atoms exposed at the particle edges. (Normally tetrahedral sheets are broken where Al is substituted for Si.) These Al atoms are known as edge sites and are capable of accepting electrons in a Lewis acid fashion.[9,32] The importance of edge sites in catalyzing the polymerization of unsaturated organic compounds is well documented.[28]

The other type of reactive site on a clay particle is on the surface of the layer and is known as a surface site. Surface sites are generally considered to be a result of isomorphous substitution of transition metals in the crystal lattice.[9,32] J.M. Thomas has demonstrated the importance of Fe^{3+} in oxidizing certain organic amines to their colored cationic derivative.[35,36] A reactive site may or may not be a cation exchange site. For instance, Fe^{3+} substituted for trivalent Al in the octahedral layer does not give rise to a cation exchange site but does constitute a reactive site since it can be reduced to Fe^{2+}. However Fe^{3+} substituted for tetravalent Si would give rise to both a reactive site and a cation exchange site. It is important to note that over 90% of the iron in montmorillonite is in the octahedral layer so that the number of dual reactive/cation exchange sites due to Fe^{3+} is rather small.

In addition to being able to act as a Lewis acid, a clay mineral can act as a Bronsted acid (proton donor).[39] This latter activity occurs naturally as clays are dried. The reactive protons are derived from the dissociation of water molecules due to polarization by exchangeable cations. The acid strength of the mineral depends upon the nature of the exchangeable cation and the percent of hydration. Clay minerals can also be "activated" to demonstrate Bronsted acidity.[10,32,39] In this case the clay mineral is washed in a strong acid solution and the primary exchangeable cation becomes H^+. Activated clays also demonstrate increasing acidity with decreasing water content. For commercially advantageous acid catalysis with clays the mineral must be nearly completely dry.[39]

Montmorillonite Catalyzed Color Reaction of Aromatic Amines

Of the many reactions catalyzed by clay minerals, the conversion of aromatic amines to their colored derivatives have been long known yet the mechanisms responsible for this type of reaction have only recently been elucidated.[29]

In the color reactions of clays both Lewis and Bronsted acidities are involved, while the adsorption of the organic molecules is controlled by electron transfer and cation exchange processes at both the edge and planar surfaces of the clay particles.[32]

The color reactions of benezidine and its tetramethyl derivative, TMB, with montmorillonite are two of the best and most widely studied systems and demonstrate the above observations quite nicely, (Fig. 2).[10,11,20,21,22] TMB is a colorless, neutral species in solution and is converted to its green derivative when brought into contact with certain clay minerals. The mechanism for this reaction is generally considered to involve an electron transfer (oxidation) from the diamine to the mineral yielding the green monovalent radical cation (TMB^+). The stability and color of this species results from conjugation of the unpaired $2p_z$ electron from nitrogen with the π electron system of the aromatic ring, reinforced by resonance involving both rings.[32] The green species exists only at a pH above 2.0. When the pH falls below 2.0 the green species

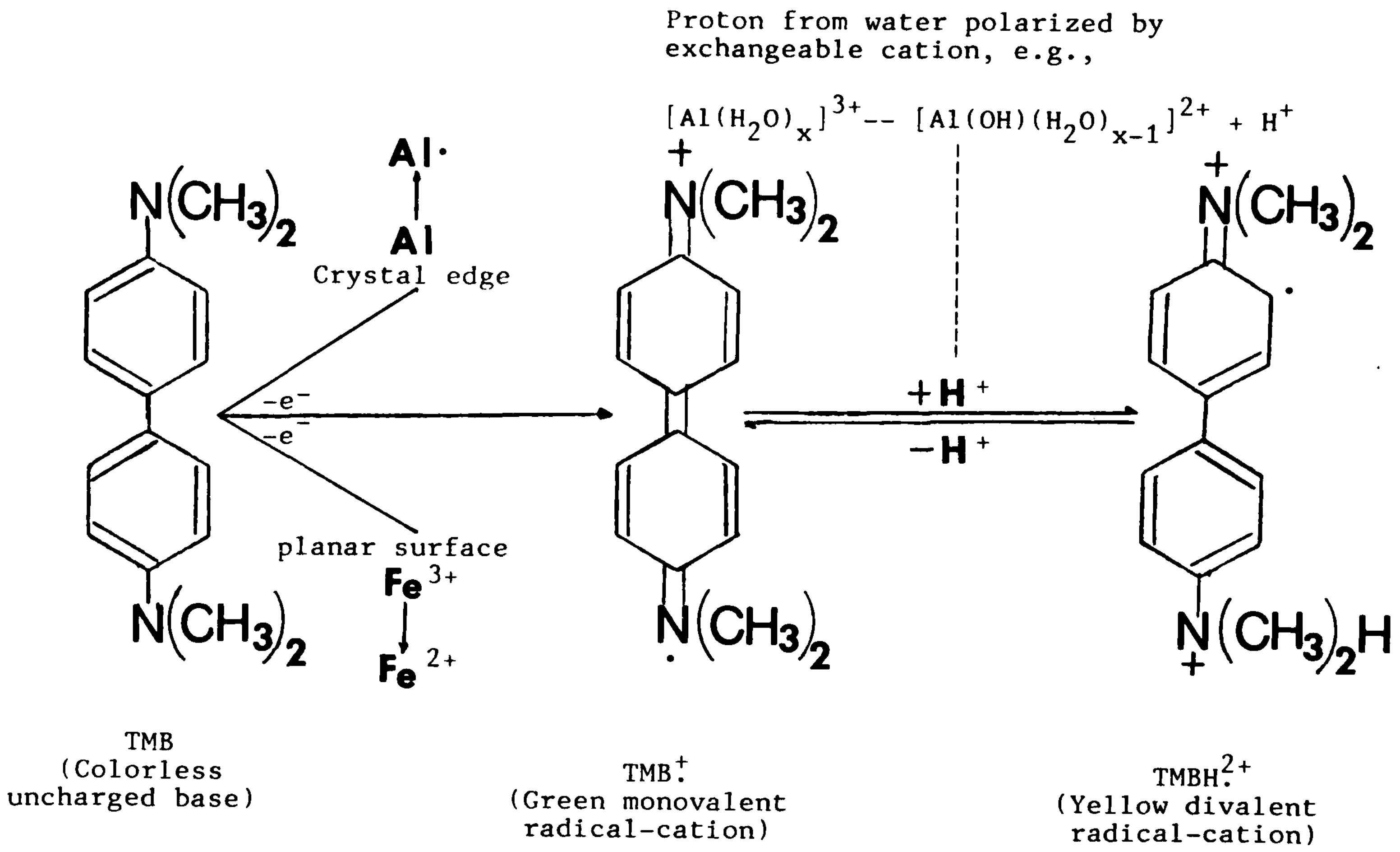


FIGURE 2. Transformation of TMB into its Colored Radical-Cation Forms Activated by Clay, Showing Effect of pH as Proposed by Theng.[31,32]

is converted to a yellow species. It was originally thought that TMB^+ accepted a proton on the lone pair of electrons of the nitrogen atom as depicted in figure 2. Though this may be a valid depiction for acid-treated or dry clay reactions with TMB, recent work by this author and others[2] has indicated that the species responsible for the yellow color at low pH values may be the result of a disproportionation reaction of aggregated TMB^+ molecules:

$$TMB^+ + TMB^+ + 2H^+ \longrightarrow TMB^{2+} + TMBH_2{}^{2+} \qquad (3)$$

and not a protonation as depicted in figure 2.

Though the evidence for this will be discussed in detail later, the structure that is responsible for the yellow color in colloidal solution, TMB^{2+}, is depicted in figure 3.

Also shown in figure 3 is the structure for TMB^+ determined by Hester[13] using resonance Raman spectroscopy. In the past the primary resonance structure for TMB^+ was thought to be the quinonal structure. However Hester has shown that the neutral nitrogen has free rotation and the N-C bond length is more characteristic of a single bond than a double bond. Therefore the most correct resonance structure for $TMB^+$is the semi-quinone type structure. The structures in figure 3 will be the ones referred to during the remainder of this paper unless stated otherwise.

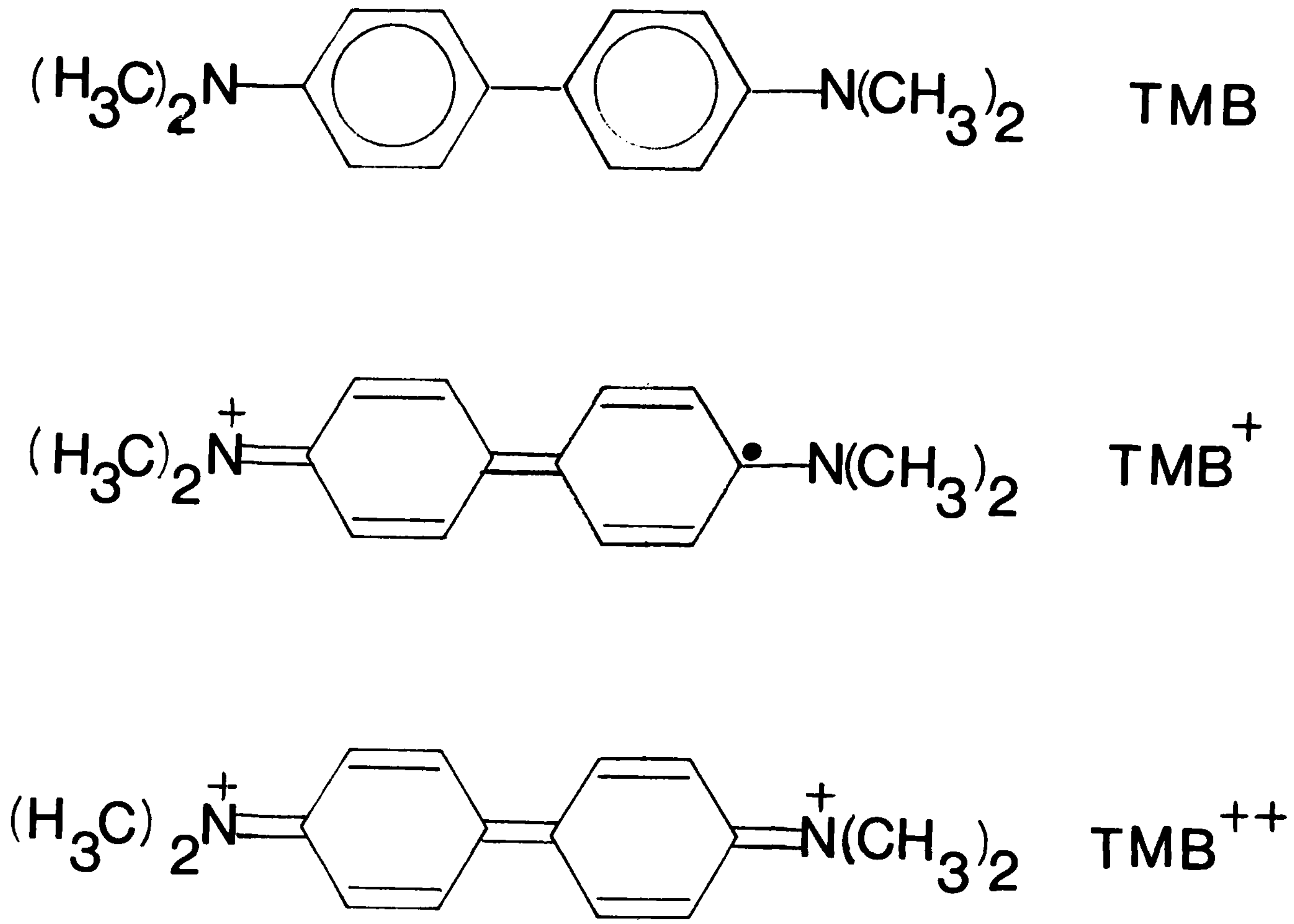


FIGURE 3. TMB Structures Discussed in Text.

The TMB/clay system has been of great importance in determining the nature of the reactive sites on the clay and the clays ability to intercalate organic molecules.[19, 35,36] Lahaw and Raziel have shown that the uptake of benezidine by montmorillonite is essentially one of cation exchange.[18] However the exchange is irreversible since the colored clay shows great stability.[32,39] This indicates that factors other than simple ion exchange are involved in the adsorption process. This system has also been of importance in determining something of the nature of the clay/ organic complex.

Hakusui et. al.,[10] have examined diffuse reflectance spectra of TMB and benezidine adsorbed on acid treated clay and have shown that both monovalent and divalent cations are present on the clay surface, pH influencing the equilibrium between the two species. Studies have shown that ion radicals can aggregate and Matsunaga[24] has concluded that electronic spectra of radical cations on clay are dependent on the mode of aggregation e.g., monomeric, dimeric or polymeric. In addition to influencing electronic spectra, a high degree of aggregation would contribute to the irreversibility of the ion exchange process and the great stability of the TMB/ clay complex.

The Basis For This Study

As indicated previously, past studies of the reaction of TMB and montmorillonite have had to rely on the use of diffuse reflection spectra and or qualitative color changes to make observations on the nature of the clay's reactivity and the nature of the amine/clay complex. The results obtained from these methods were sometimes inconclusive or questionable since the spectra had to be taken on dry or nearly dry samples of colored clay. As described earlier, the drying process changes the reactivity of the clay and many times more than one species of amine derivative were detected.[10,11,24]

The ability to study the reaction in colloidal solution was thought to offer many advantages. The small size of the montmorillonite colloidal particle, 1500 Å radius, reduces light scattering and produces a slightly turbid sample which is nearly transparent in the visible and gives clear and sharp absorption spectra.

The nature of the spectra obtained permitted observation of the reaction under fully hydrated conditions. Furthermore, since catalytic efficiencies are known to increase with decreasing particle size, the ability to produce small colloidal particles increases the surface area available for reaction and permitted the observation of intense color changes using low concentration of TMB and montmorillonite.

Finally the relatively transparent nature of the montmorillonite colloid allowed the use of laser flash photolysis techniques to study the kinetics of the TMB/clay reaction. This kind of kinetic study has not been previously reported.

CHAPTER II

EXPERIMENTAL

Instrumentation

Absorption spectra were obtained on a Perkin-Elmer model 552 UV-VIS spectrophotometer. Electron paramagnetic resonance (EPR) spectroscopy experiments were conducted on a Varian E-line series EPR spectrometer. Colloidal particle sizes were measured on a Nicomp HN5-90 dynamic light scatter spectrometer. Centrifugations were conducted on a Sorvall SS-3 superspeed centrifuge.

Laser flash photolysis studies were conducted with a Lambda Physik X100 excimer laser, filled with a Xenon/chlorine gas mixture capable of delivering a 308 nm pulse. The duration of the pulse is 12 ns (FWHM) and is delivered with an energy of 80-100 mJ. The signal emanating from the photomultiplier tube was captured by a Tektronix 7912 AD programmable digitizer transient waveform unit. This unit was interfaced with a Tektronix 4052A computer for data processing and display. The apparatus display is on figure 4.

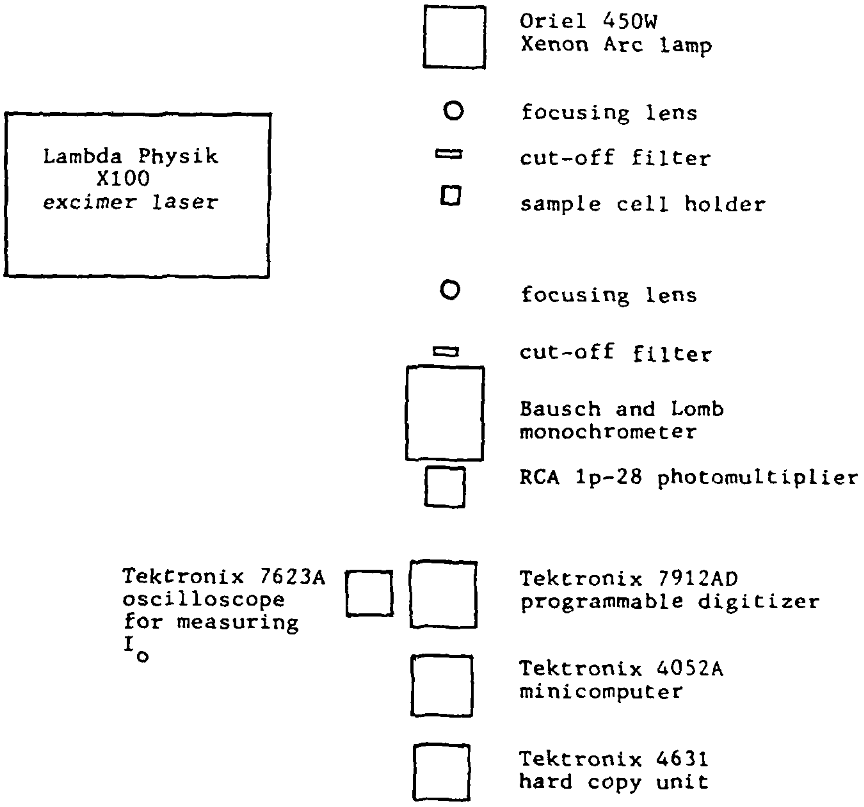


FIGURE 4. Diagrammatic Sketch of Laser and Computer Assembly.

Chemical

N,N,N',N', - Tetramethylbenzidine (Aldrich), N,N,N',N', - Tetramethyl p-Phenylaminediamine Dihydrochloride (Eastman), Sodium Chloride (Fisher), Sodium dodecylsulphate (B.D.H. Chemicals Ltd.), and Sodium Hydrosulfite (Fisher) were used as supplied. N,N' - dimethyl - 4,4 - bipyridinium dichloride (Aldrich) was recrystallized from methanol three times. The primary solvent used for this work, ethanol and water (1:1 v/v), was prepared with reagent quality absolute ethanol (AAPER Alcohol Co.) and distilled/deionized water.

Colloidal Montmorillonite Preparation

The montmorillonite used in this work was obtained from the Georgia Kaolin Company as the pure mineral. The Na^+ exchanged form was prepared by mixing the clay sample several days with 1$\underline{N}$ NaCl. This was followed by several washings with distilled water and centrifugation cycles to remove the excess sodium chloride and other exchangeable ions from solution. The clay was then resuspended and dialyzed until a negative chloride test was obtained with 0.1 $\underline{M}$ $AgNO_3$.

Technical data supplied by Georgia Kaolin Co. indicated the CEC of montmorillonite was 100meq/100g and the chemical analysis is as depicted on Table 1.

The clay colloids were made by dispersing the mineral with a high shear Waring blender for approximately five

TABLE 1

CHEMICAL ANALYSIS OF MONTMORILLONITE

% SiO_2	58.6
Al_2O_3	21.2
Fe_2O_3	0.97
TiO_2	0.23
CaO	2.42
MgO	3.79
Na_2O	4.07
K_2O	0.37

minutes. This was normally followed by five minutes of sonication. The particles had an average hydrodynamic radius of 1500-2000 Å and consisted of 3 to 4 layers (Na^+ exchanged form).[9,32]

The convenient CEC (1meq/1g) provided an easy measure of the amount of clay dispersed in solution. 1 gram of montmorillonite suspended in one liter of water gave a "concentration" of cation exchange sites of 10^{-3} equivalents/liter normally expressed as 1meq/L.

Sample Data and Calculations

Transients produced in a pulsed laser experiment can follow a number of decay processes. For the TMB system under study these processes are primarily first or second order.

A typical first order process is the decay of the excited TMB triplet state (TMB^T). The concentration of TMB^T is found to follow a first order exponential decay:

$$[TMB^T]_t = [TMB^T]_o \exp(-kt) \qquad (4)$$

The concentration of TMB^T is related to the amount of light adsorbed following the laser pulse by Beer's law:

$$A = \epsilon cl \qquad (5)$$

where

A = absorbance or optical density (OD)
ϵ = extinction coefficient
c = concentration of TMB^T
l = cell length (usually 1 cm)

The laser and computer assembly described previously can monitor the change in adsorbance versus time by relating it to the change in intensity of adsorbed light:

$$I_t = I_o \exp(-kt) \tag{6}$$

or rewritten

$$\ln = (I_o/I_t) = kt \tag{7}$$

Figure 5 shows the decay of a typical transient versus time. The Tektronix 4052A has been programmed to compute the optical density of TMB^T at any time, t, by the following equation:

$$\log (I_o/(I_o - I_{t'})) = OD \tag{8}$$

Since OD is proportional to $[TMB^T]$ then:

$$\log (I_o/(I_o - I_{t'})) \propto [TMB^T] \tag{9}$$

A plot of ln $[TMB^T]$ versus time will yield a straight line of slope k where k is the first order rate constant. The computer will perform the calculation:

$$\ln (\log (I_o/(I_o - I_{t'}))) \text{ vs time} \tag{10}$$

which yields a straight line plot as indicated on figure 6. The first order rate constant for the decay of TMB^T can be computed by determining the slope of the line between

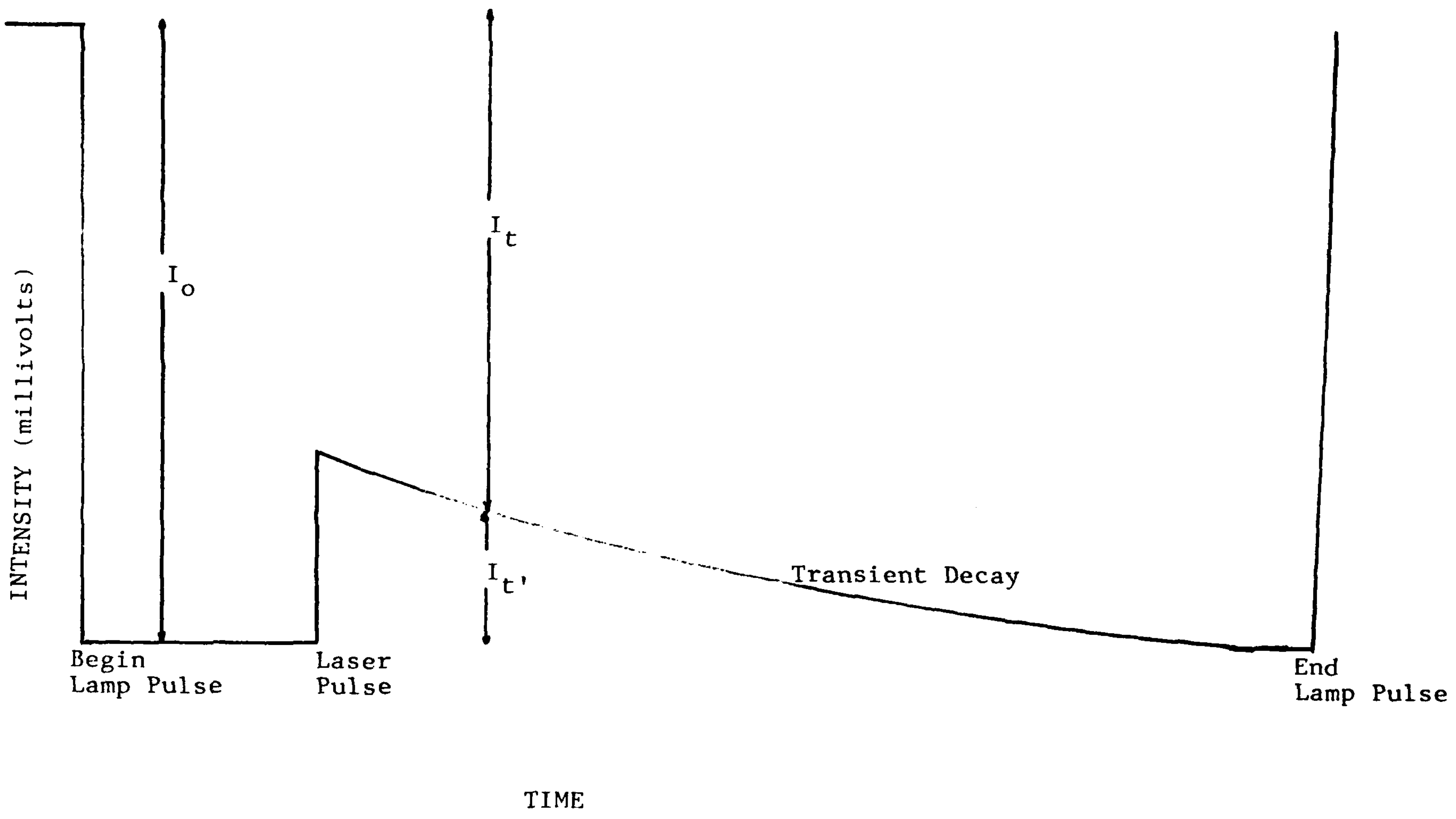


FIGURE 5. Diagrammatic Sketch of Typical Transient Decay Measured and Quantified by Tektronix Computer Assembly.

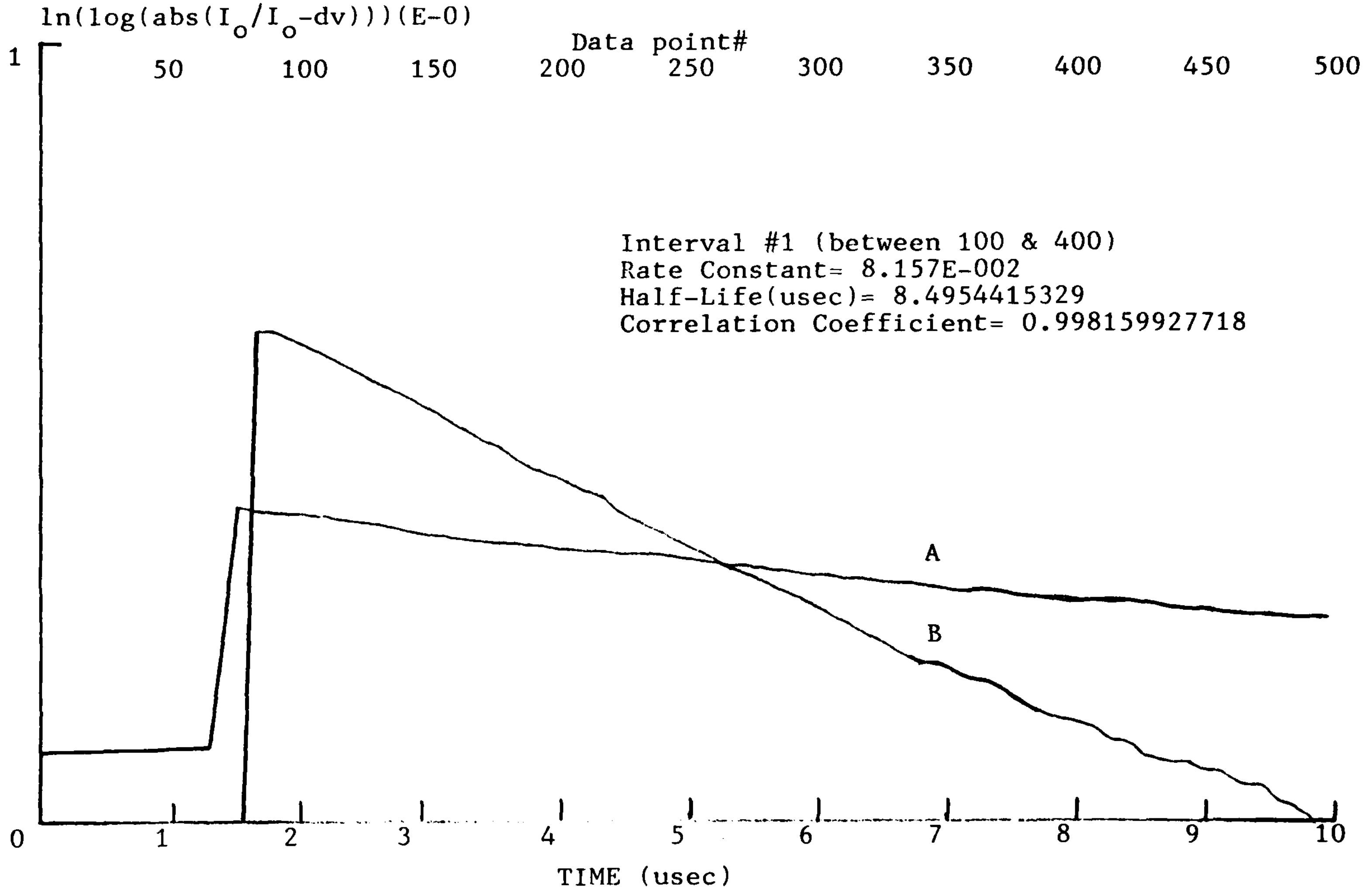


FIGURE 6. Computerized Decay Curve (A) and Log Plot (B) of TMB^T Produced by Laser Photolysis of $1x10^{-4}$ M TMB in Deoxygenated Ethanol.

various data points. This computation is performed by the 4052A and printed out as indicated. The concentration of TMB^T at any time, t, can be determined as follows:

$$[TMB^T]_t = \log (I_o/(I_o-I_{t'}))/\epsilon l \qquad (11)$$

Though the value of $[TMB^T]$ is not essential to determine the rate constant by the above method it is helpful in determining the percentage of transient produced relative to the initial concentration of starting material.

The lifetime of the TMB^T transient can be quenched by adding various substances (quenchers) to the system. If the transient is assumed to undergo decay via processes independent of the presence of quencher, then the effect of quencher can be readily determined from the relationship:

$$k = k_o + k_q\,[Q] \qquad (12)$$

where

k = overall decay rate constant

k_o = decay rate constant in the absence of quencher

k_q = quenching rate constant

$[Q]$ = quencher concentration

A plot of k versus [Q] as in figure 8 will yield a straight line of slope k_q.

The system depicted in figures 6,7, and 8 is the 308 nm laser photolysis of TMB in deoxygenated ethanol. Alkaitis and Grätzel[1] have shown that the primary photoreaction in organic

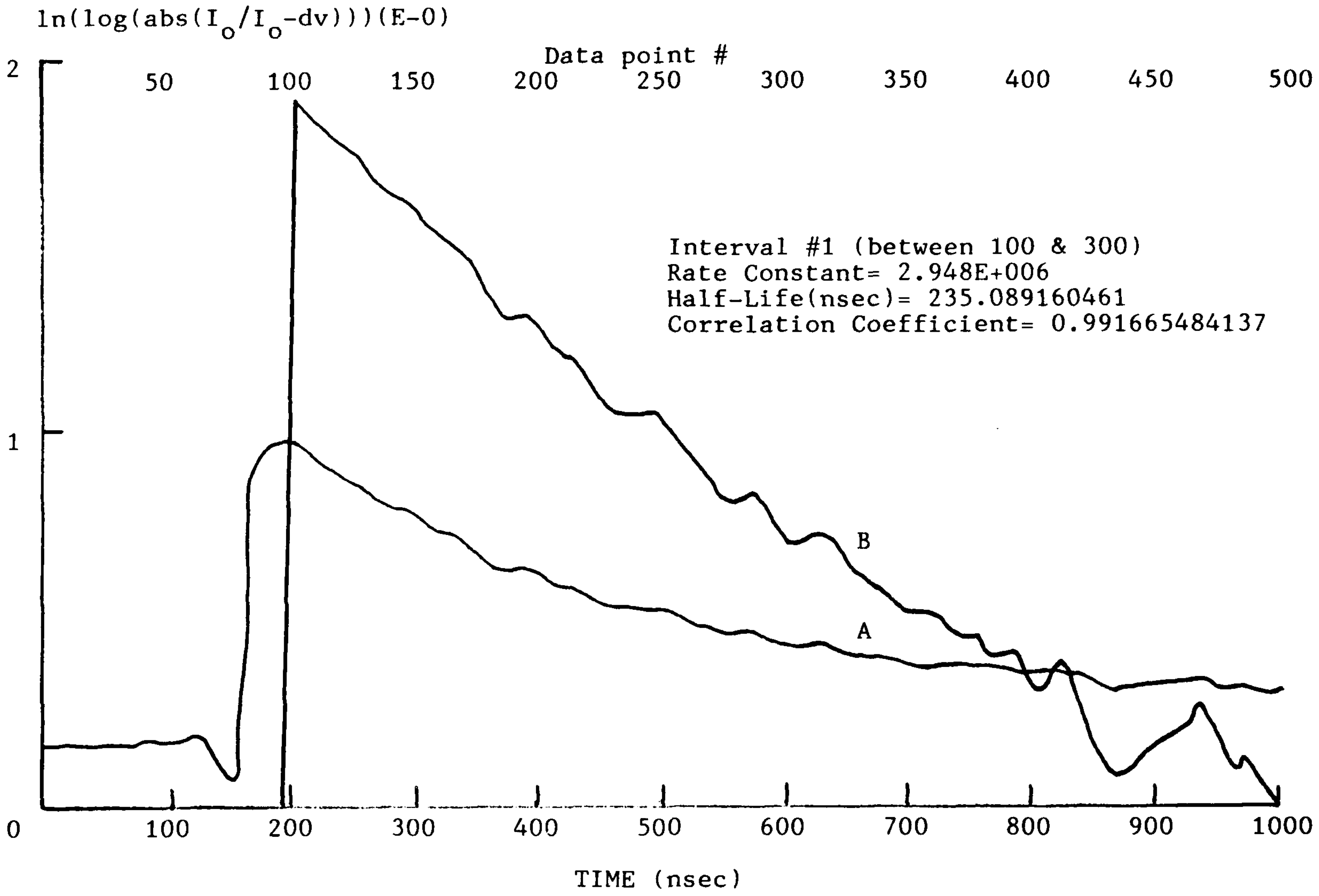


FIGURE 7. Computerized Decay Curve (A) and Log Plot (B) of TMB^{T} Produced by Laser Photolysis of 1x10^{-4}M TMB in Deoxygenated Ethanol in the Presence of 1x10^{-3}M Eu^{3+}.

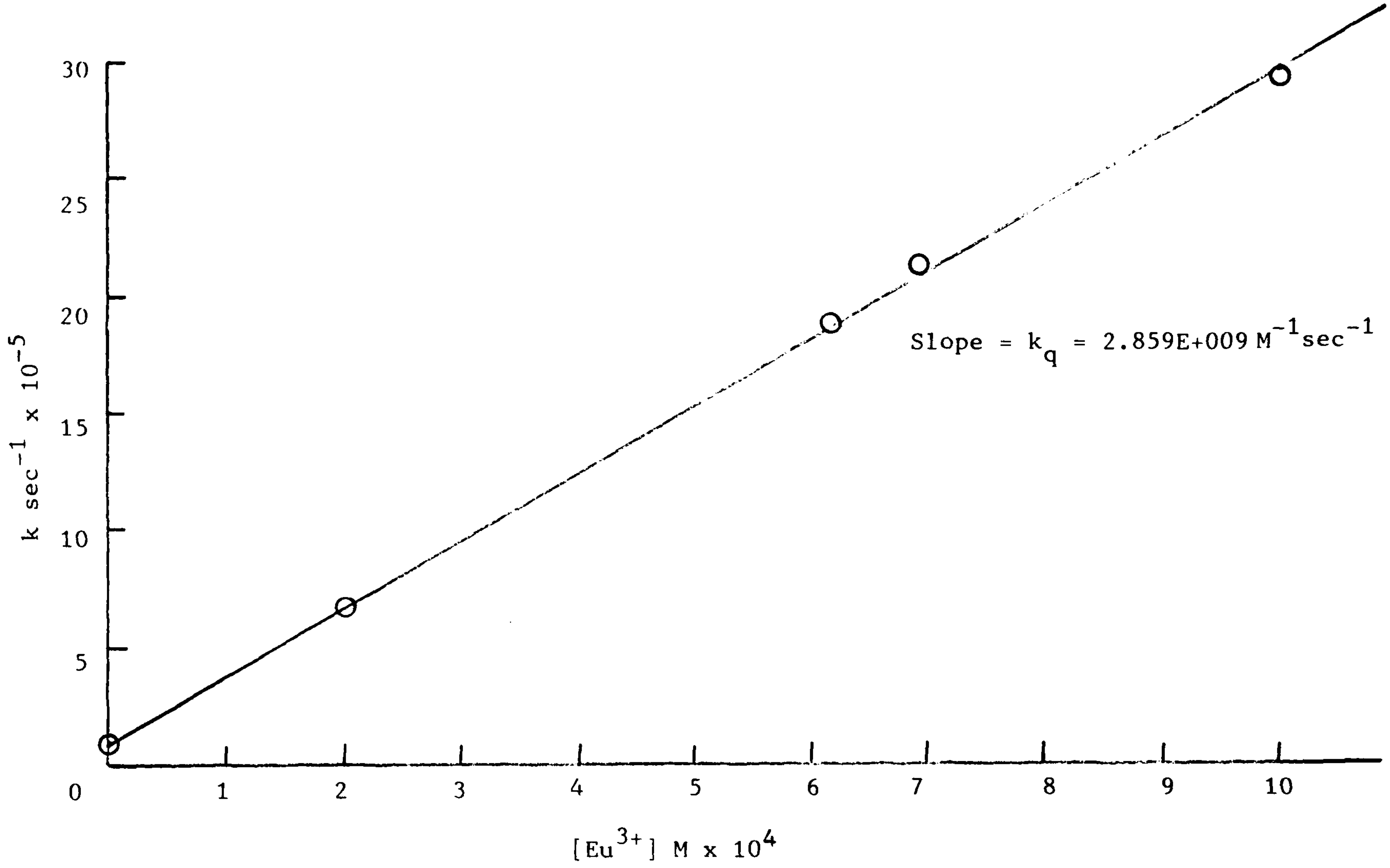


FIGURE 8. Plot of Lifetime Data to Determine Quenching Rate Constant for the Quenching of TMB^T by Eu^{3+}

solvents is triplet formation.[1] The triplet is known to transfer an electron to Eu^{3+} and the quenching rate constant k_q for the reaction is $2.86 \times 10^{-9}\ M^{-1}\ s^{-1}$, determined by the method described above.

In more ionic solvents, i.e., $EtOH/H_2O$ (1:1,v/v), at high laser intensity the primary transient produced is the monovalent radical cation of TMB.

The process for the decay of TMB^+ is:

$$TMB^+ + TMB^+ \longrightarrow TMB + TMB^{++} \qquad (13)$$

and follows a second order decay:

$$1/[TMB^+]_t - 1/[TMB^+]_o = kt \qquad (14)$$

By relating the $[TMB^+]$ to the intensity of adsorbed light as before and plotting 1/OD vs t the laser and computer assembly can produce a second order plot as shown on figure 9.

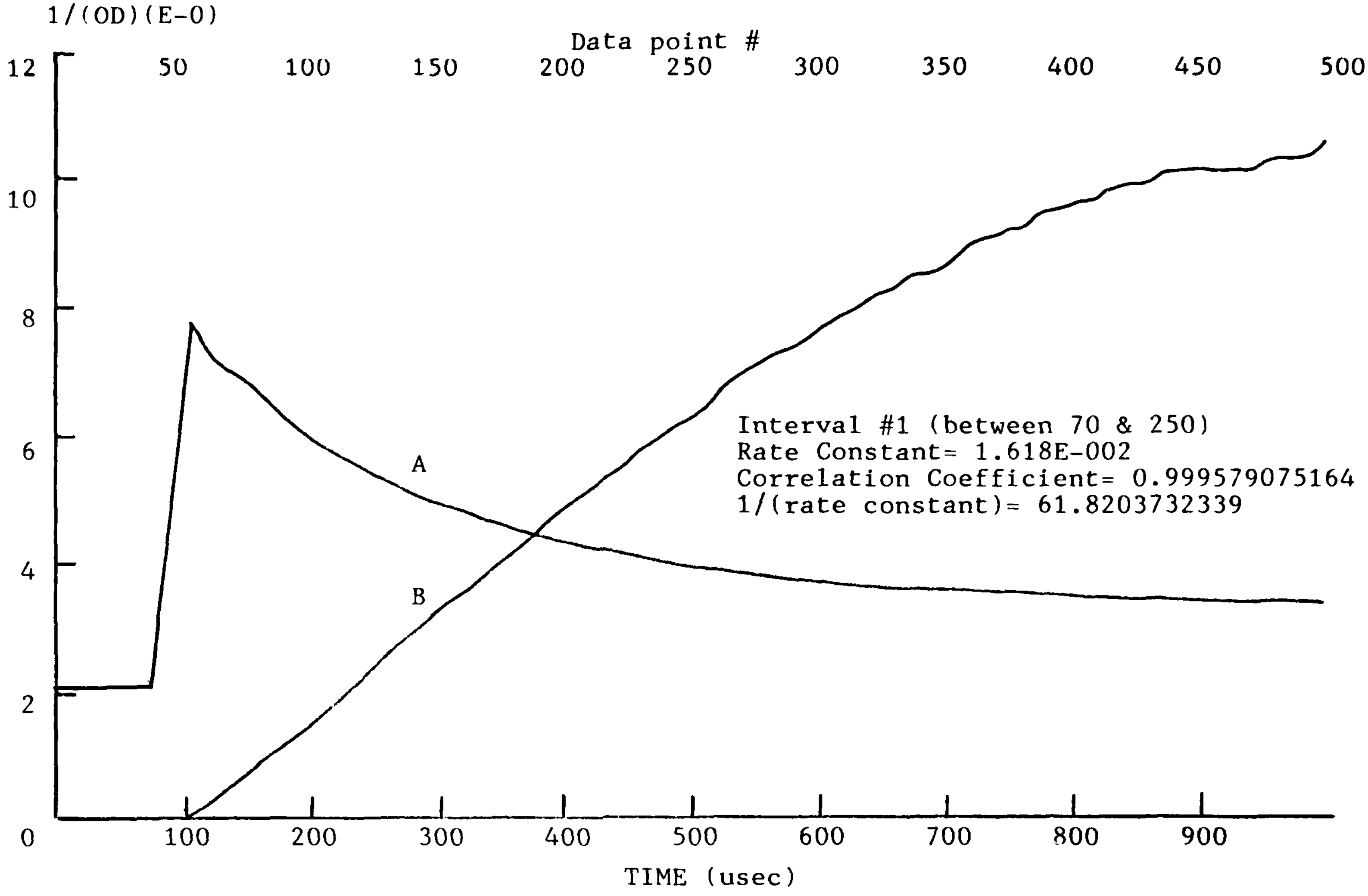


FIGURE 9. Computerized Decay Curve (A) and Log Plot (B) of TMB^+ Produced by High Intensity Laser Photoionization of $1x10^{-4}$M TMB in $EtOH/H_2O$ (1:1 v/v).

CHAPTER III

RESULTS AND DISCUSSION

Environmental Effect on TMB Protonation Equilibria

The nature and physical location of TMB in solution is known to change as a function of pH and solvent. This change can be monitored through analysis of electronic absorption spectra.

Figure 10 shows the absorption spectra of 10^{-4}M TMB in an ethanol and water (1:1 v/v) solution as a function of pH. Three different spectra are distinguishable as the pH is lowered in accord with the reactions:

$$\mathrm{TMB} \underset{K_1}{\overset{+H^+}{\rightleftharpoons}} \mathrm{TMBH}^+ \underset{K_2}{\overset{+H^+}{\rightleftharpoons}} \mathrm{TMBH_2}^{2+} \qquad (15)$$

In neutral or basic solutions (to pH 10.0) the primary species in solution is neutral aromatic TMB which has an absorption peak near 300 nm. In acidic media the primary species is protonated TMB, TMBH^+, which has an absorption maximum near 310 nm. $\mathrm{TMBH_2}^{2+}$ exists in very acidic media and its absorption maximum is near 250 nm.

Beck and Brus[2] have measured the protonation behavior of TMB in SDS micellar solution and have shown a significant solvent effect. As in EtOH:H_2O solution three forms of TMB exist and the λ_{max} positions show small solvent shifts. The significant change is that the SDS solvation has

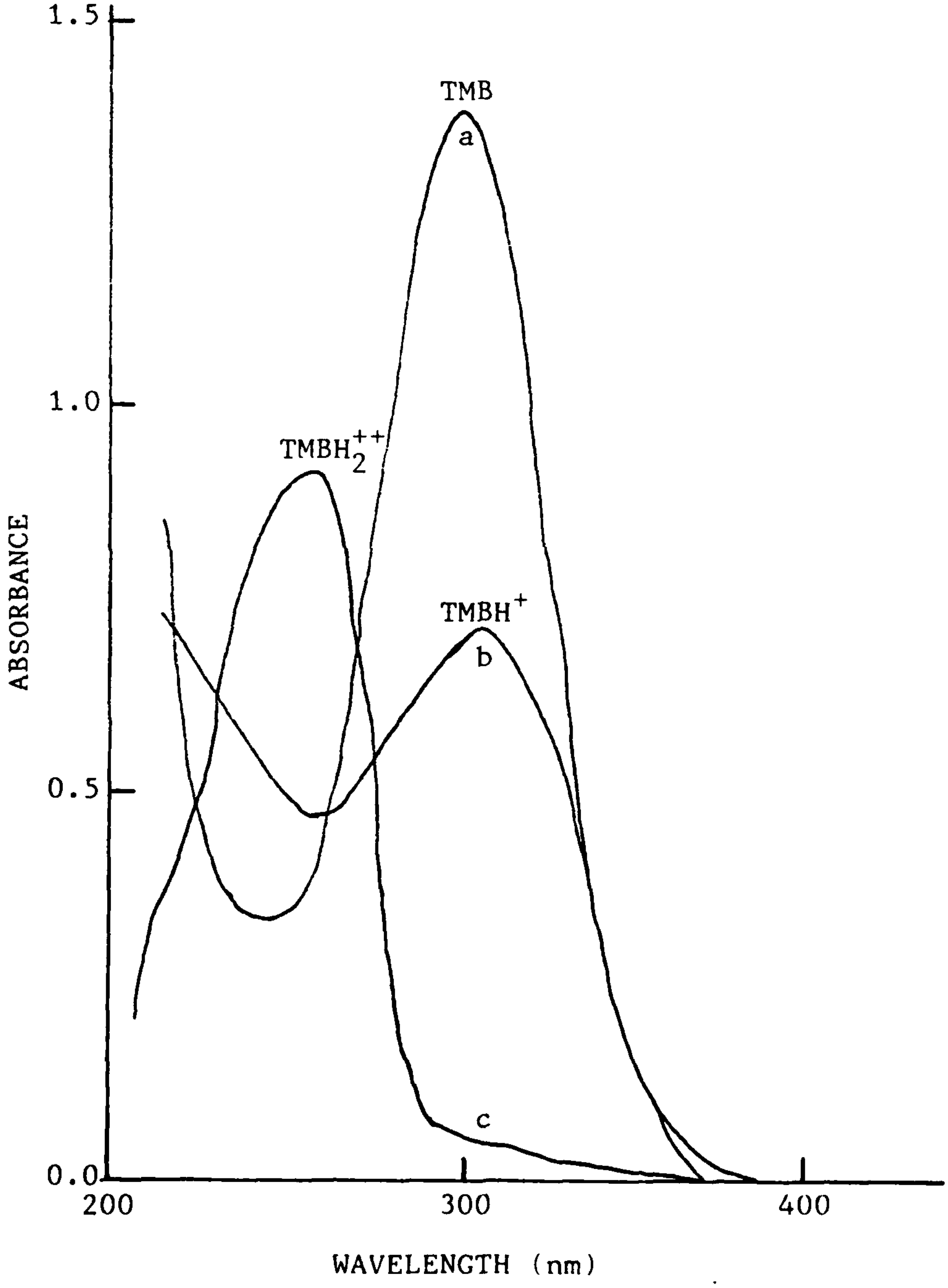


FIGURE 10. Absorption Spectra of 1×10^{-4}M TMB in EtOH/H_2O (1:1 v/v) as a function of pH. Curve A pH=7.3, Curve B pH=3.4, Curve C pH=1.8.

shifted the equilibria towards the protonated forms at lower H^+ concentration as indicated by a change in the pK_a values; $pKa_1 = 4.0$, $pKa_2 = 3.1$ for MeOH and $pKa_1 = 6.0$ and $pKa_2 = 4.2$ for SDS.

TMB has negligible solubility in pure water at pH 7.0. At low pH values, usually less than 2.0, TMB will dissolve as $TMBH_2^{2+}$ as shown by absorption data. If OH^- is added to this solution TMB will precipitate as the pH is raised above 2.0, the presence of TMB^+ never being detected. This behavior as well as studies in their lab have lead Beck and Brus to conclude that in micellar solution TMB or $TMBH^+$ is located in the micellar interior or on the surface while $TMBH_2^{2+}$ is located in the aqueous phase.

TMB$^+$ Reference Absorption Spectra

As indicated previously, most work done on the reaction of aromatic amines and their derivatives with montmorillonite relied heavily upon qualitative color changes and/or diffuse reflection spectra to make comments on the nature of the organo/clay complex. For instance, many works provide tables that indicate an amount of coloration, i.e., green, dark green, light green, etc., to indicate the extent to which TMB$^+$ is formed on various types of clays under different conditions.[18,19,20] Hasegawa[11] and others[10,24] have provided diffuse reflection spectra of TMB$^+$ on dry or slightly moistened montmorillonite. However these, like qualitative color changes, proved too imprecise to provide information on the interfacial processes at the clay surface and between its layers. Since use of colloidal montmorillonite was anticipated to provide enlightening data, the investigation begins with a report of absorption spectra of TMB$^+$ adsorbed on colloidal montmorillonite and a comparison of this data with that obtained through previously monitored methods.

Figure 11a shows the absorption spectrum of an ethanol/water solution (1:1 v/v) of TMB$^+$ obtained from oxidizing $1X10^{-4}$M TMB with dilute bromine water. This spectrum with an absorption maximum at 470 nm and two smaller peaks at 460 nm and 440 nm agrees well with literature references for TMB$^+$ in homogeneous solution and SDS micelles.[1,30]

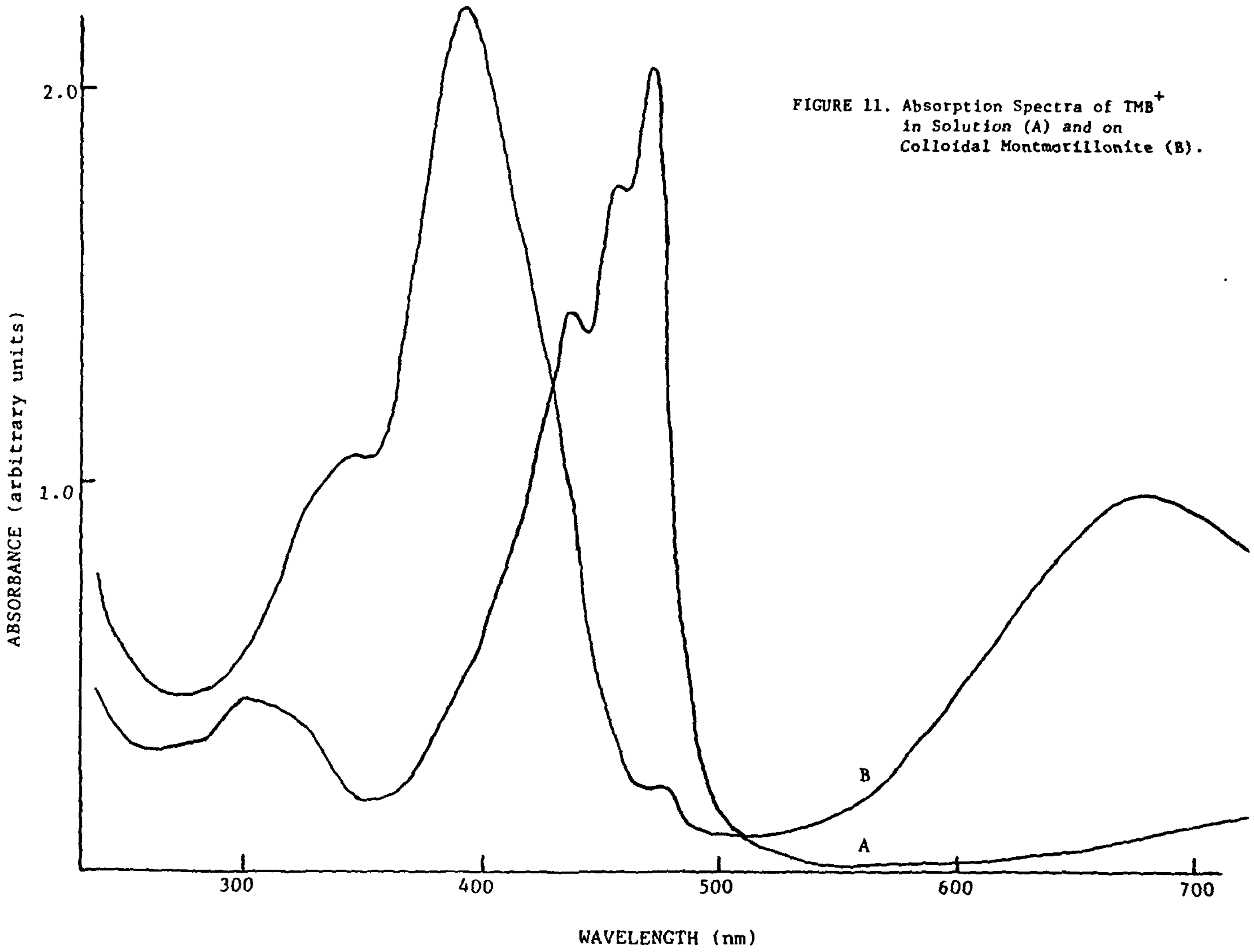


FIGURE 11. Absorption Spectra of TMB^+ in Solution (A) and on Colloidal Montmorillonite (B).

The peak at 300 nm is due to non-oxidized TMB. This solution was clear prior to the addition of Br_2H_2O and turned a dark yellow upon the addition of the oxidizer. This was a slight discrepancy with literature references to TMB^+ since it is always considered to be a green species. However concentrations in excess of $1X10^{-2}M$ TMB appear more greenish than yellow upon oxidation. This discrepancy in the subjective determination of the color of TMB^+ in solution indicated that a re-examination of the classic TMB/clay reaction might provide new or previously unreported information.

Figure 11b is the absorption spectrum of TMB^+ on colloidal montmorillonite. This spectrum was obtained by mixing an ethanol/water solution containing $1X10^{-4}M$ in TMB with 1 meq/L of montmorillonite prepared by the method described previously. This solution was allowed to mix in ordinary room light for approximately 12 hours to insure complete thermal reaction of TMB. The color of the solution was dark green agreeing well with literature values indicating a strong or complete reaction of TMB.[26] This was expected due to the high CEC of the montmorillonite used in the experiment. A confirmation of this was obtained following centrifugation of the clay. After centrifugation the clay was green and the supernatant liquid clear. An absorption spectrum of the supernatant gave no indication of the presence of any TMB species indicating complete reaction of TMB with montmorillonite.

The spectrum of the TMB/clay complex shows a primary absorption peak at 390 nm, a broad absorption at 680 nm and two smaller peaks or shoulders at 475 nm and 340 nm. The peaks at 390 nm and 680 nm agree well with literature values for the absorption maximum of the TMB^+ dimer.[30] The smaller peaks have never been previously reported.

Dimerization of Organic Aromatic Cations on Colloidal Montmorillonite

The fact that the primary absorptions for the TMB/clay complex were at 390 nm and 680 nm lead to the observation that the primary mode of interaction for TMB^+ molecules on colloidal montmorillonite was by-pairs. Since previous works[10,24] have shown that the collective interaction for organic cations can be more-than-by-pairs on dry and/or acid clay surfaces, it was necessary to investigate the mode of interaction of other aromatic organic cations to determine if a generalized statement could be made concerning their interaction on colloidal montmorillonite.

N,N,N',N', - Tetramethyl p- Phenylaminediamine (TMPD), also known as Wursters Blue, has been widely studied and spectra of $TMPD^+$ in solution and in the solid state are well characterized.[15,38] Hausser and Murrell[12] first suggested dimer formation for $TMPD^+$ at low temperatures and based their calculations on the fact that complexes are formed between two $TMPD^+$ molecules lying in parallel planes, one above the other. Uemura, et. al.,[38] have shown that in solution a monomer-dimer equilibrium exists for TMPD cation-radicals, the dimer taking precedence at lower temperatures or higher concentration. Iida and Matsunaga[15] have examined solid Wurster salts and have shown collective interaction of $TMPD^+$ molecules through use of diffuse reflection spectra.

Figure 12b shows the absorption spectrum of $TMPD^+$ in ethanol/water obtained from the oxidation of $1X10^{-4}M$ TMPD by dilute bromine water. This spectrum agrees well with literature references for the $TMPD^+$ monomer. Figure 12a shows the absorption spectrum of a TMPD/clay complex obtained from mixing $1X10^{-4}M$ TMPD in ethanol/water with 1 meq/L of montmorillonite prepared by the method described previously. This spectrum agrees well with literature references for the $TMPD^+$ dimer. It is interesting to note that the TMPD/clay complex very closely resembles reported spectra for the $TMPD^+$ dimer in low temperature solution.[38] This is in contrast to the TMB/clay complex (figure 11b) which has features not recorded in reference spectra of the TMB^+ dimer in low temperature solution. Although there are no reported spectra of $TMPD^+$ on clay for comparison with figure 12b it would seem that the mode of interaction of $TMPD^+$ molecules on colloidal montmorillonite is by-pairs and that the $TMPD^+$/clay complex is free of any other type of interaction and/or TMPD species, other than TMPD dimers.

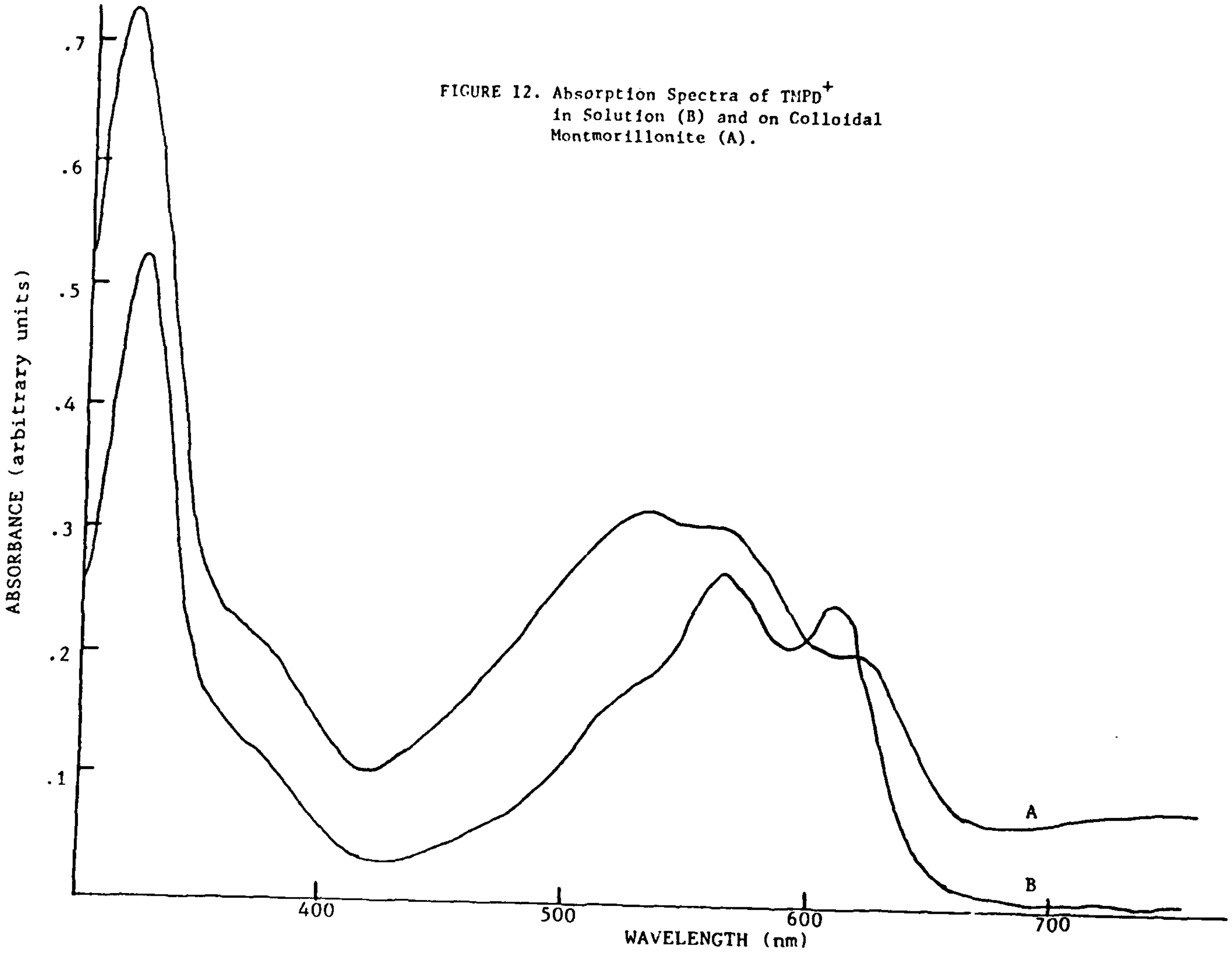


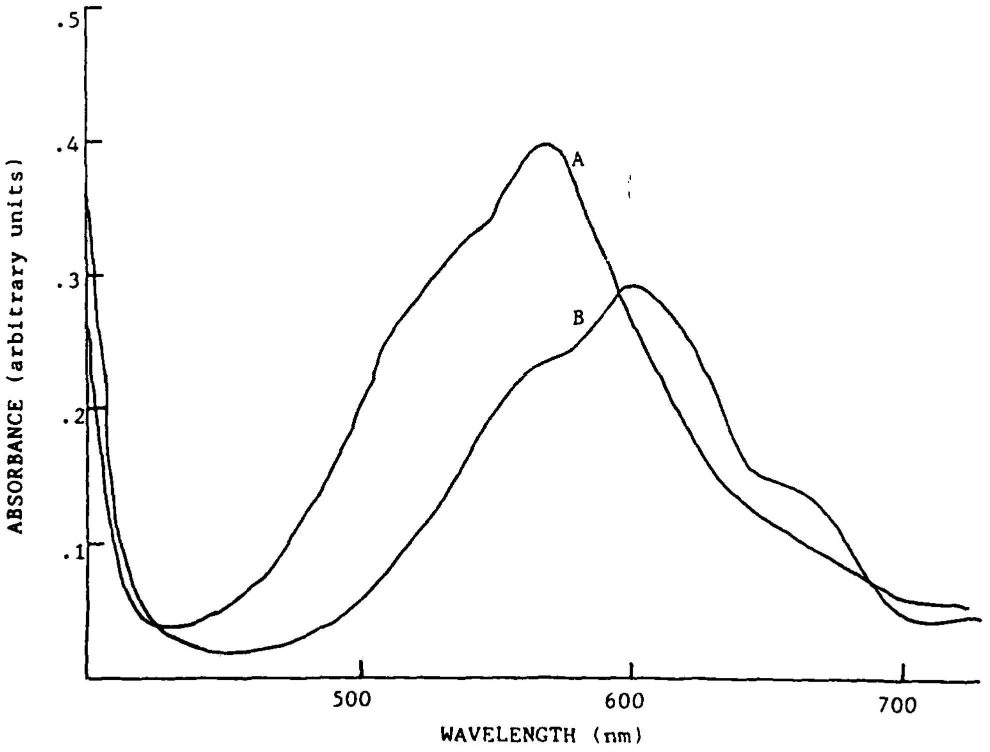
FIGURE 12. Absorption Spectra of $TMPD^+$ in Solution (B) and on Colloidal Montmorillonite (A).

Another aromatic organic cation which has a well characterized dimer is N,N' - dimethyl - 4,4' bipyridinium dichloride, better known as methyl viologen (MV). Methyl viologen exists in solution in its oxidized form, MV^{2+}. In deoxygenated solution and in the presence of an appropriate reducing agent, MV^{+} can be formed. The reduced form of methyl viologen is characterized by its deep blue color.

Figure 13b shows the absorption spectrum of MV^{+} formed by reducing a $1X10^{-4}M$ deoxygenated solution of methyl viologen with sodium hydrosulfite. This solution was deep blue and the spectrum is characteristic of a MV^{+} monomer. Figure 13a shows the spectrum of a MV^{+}/clay complex formed by adding 1 meq/L of montmorillonite to a reduced, deoxygenated solution of $1X10^{-4}M$ methyl viologen. Although montmorillonite has a limited electron donating capability,[28] the presence of montmorillonite alone was not sufficient to reduce MV^{2+} and sodium hydrosulfite had to be added to the solution prior to the addition of montmorillonite. The MV^{+}/clay complex was purple in color and the spectrum agrees well with literature references to the MV^{+} dimer.[6,16,25]

Absorption spectroscopy seems to indicate that the primary mode of interaction of aromatic organic cations is by-pairs. DellaGuardia[3,4] has shown that organic cations tend to aggregate on colloidal montmorillonite particles and this would lead to the assumption that the collective interaction demonstrated by TMB^{+}, $TMPD^{+}$, and MV^{+} is a

FIGURE 13. Absorption Spectra of MV^+ in Solution (B) and on Colloidal Montmorillonite (A).



concentration effect. If it is assumed that all the radical-cations in a $1X10^{-4}M$ bulk solution are intercalated in the clay particles of a 1 meq/L montmorillonite colloid then the effective local concentration could be as high as $1.82X10^{-1}M$ (appendix 2). However this concentration effect would not account for the fact that the TMB/clay complex absorption spectrum has peaks or shoulders not associated with TMB^+ in dimeric or polymeric degrees of aggregation. These peaks therefore must be due to forms of TMB other than TMB^+ dimers.

TMB^{2+} Reference Absorption Spectra

In order to analyze the absorption spectrum of the TMB^+/clay complex it was necessary to obtain a spectrum of a colloidal complex at low pH. Since clays have an inherent acidity associated with them it was believed that the absorptions at 475 nm and 340 nm might be due to forms of TMB associated with low pH, i.e., TMB^{2+}, $TMBH^+$, or $TMBH^{2+}$, even though the TMB/montmorillonite complex absorption spectrum was obtained in a neutral solution, pH 7.0.

Figure 14b shows the absorption spectrum of TMB^{2+} obtained by lowering to pH 1.8 the ethanol/water solution of $1X10^{-4}M$ TMB oxidized by dilute bromine water. The TMB^{2+} moiety is yellow-orange in color and has an absorption maximum at 475 nm. The peak at 250 nm is consistent with the absorption maximum for $TMBH_2^{2+}$. These results are consistent with the observation of Beck and Brus[2] for the

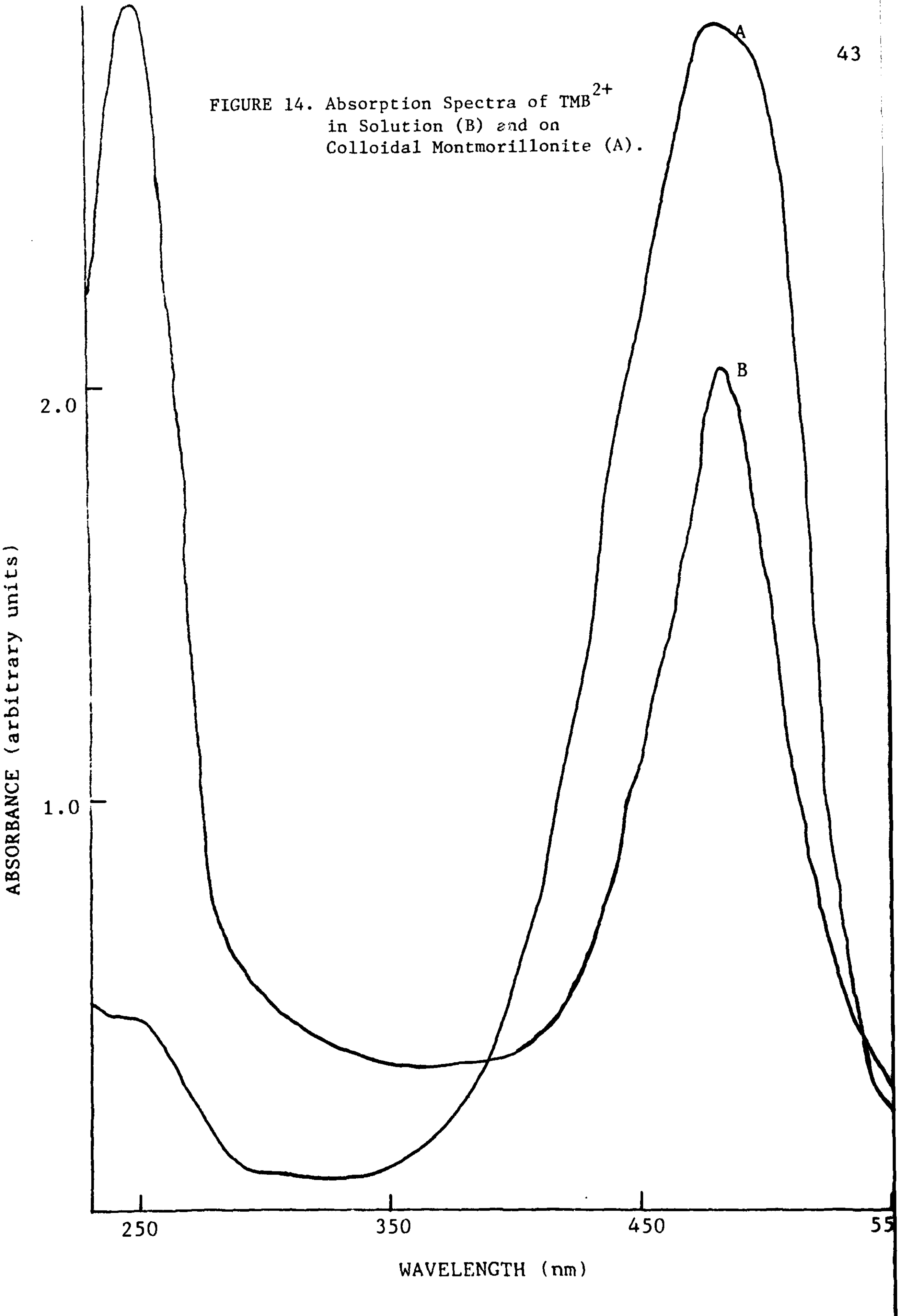


FIGURE 14. Absorption Spectra of TMB^{2+} in Solution (B) and on Colloidal Montmorillonite (A).

net disproportionation reaction of TMB^+ in acidic media depicted in equation 3. It should be noted at this time that dilute bromine water can oxidize $TMBH_2^{2+}$ to TMB^{2+} directly:

$$TMBH_2^{2+} + Br_2 \longrightarrow TMB^{2+} + 2HBr \qquad (16)$$

giving an absorption spectrum identical to that depicted in figure 14b.

Figure 14a shows the absorption spectrum obtained from the addition of 1 meq of montmorillonite to an ethanol/water solution of $1X10^{-4}M$ TMB at pH 1.8. The resulting colloidal solution was yellow in color and its spectrum appears identical to that of TMB^{2+} in solution. This was not expected since the species responsible for coloring montmorillonite yellow was thought to be the divalent radical cation, $TMBH^{2+}$. To investigate this further a green colored colloid was prepared as indicated in the previous section and was then made highly acidic (pH 1.5). The color of the colloid slowly changed from green to yellow. When the color transformation appeared complete an absorption spectrum indicated the same results depicted in figure 14a. Since the TMB^{2+} moiety in acidic solution results from a disproportionation reaction, one may envision a disproportionation of the TMB^+ dimer on the acidified green colored colloid as follows:

$$\underset{\text{green}}{(TMB^{+})_2} + 2H^{+} \longrightarrow \underset{\text{yellow}}{TMB^{2+}} + TMBH_2^{\,2+} \qquad (17)$$

This would also appear to be a valid depiction of the color change associated with acid clays and would account for the fact that TMB moieties other than TMB^{+} dimer are detected in the diffuse reflection spectra of dry or nearly dry clay complexes of TMB.

Also interesting were the results obtained following centrifugation of the TMB^{2+}/clay complex. The clay was yellow and the supernatant clear. An absorption spectrum of the supernatant showed no TMB moiety of any kind. This means that any $TMBH_2^{\,2+}$ detected by absorption spectroscopy of the yellow clay colloid was present on the clay particle surface or in the layers and not in the aqueous phase. As mentioned earlier, $TMBH_2^{\,2+}$ in micellar solution always resides in the aqueous phase and not on the micellar interior or on the surface. This is further evidence for the unique ability of montmorillonite to intercalate organic molecules and verifies that these molecules are so tightly bound that they cannot be removed from the clay under most circumstances.

Analysis of the absorption characteristics of the TMB^{2+}/clay complex seems to indicate the presence of a limited amount of TMB^{2+} on the clay particle surface of a TMB/clay colloid at neutral pH. However it may be argued that the absorption at 475 nm on the TMB^{+}/clay complex is due to the presence of TMB^+ monomer since its absorption maximum is 470 nm, close to that of TMB^{2+}.

The Influence of pH on the Absorption Spectrum of a TMB/Montmorillonite Complex

In order to positively conclude that the absorption peak at 475 nm of the TMB/clay colloid is due to the presence of a limited quantity of TMB^{2+} it was necessary to monitor the change in the absorption spectrum of a TMB^+/clay complex with changing pH.

Figure 15 depicts the effect of changing pH on the TMB^+/clay complex absorption spectrum. Figure 15a shows the characteristic spectrum of the TMB/clay complex near neutral pH and agrees well with the reference spectrum, figure 11b. Figure 15b is the absorption spectrum of the same colloidal solution as 15a with HCl added to lower the pH to 3.4. This spectrum has many interesting features but it is important to note at this time the growth of the absorption peak at 475 nm. This peak is even more prominent in figure 15c. This absorption spectrum is obtained from the colloidal solution depicted in figure 15b after lowering the pH to 1.8. One point to note is that the spectrum at figure 15b was taken approximately 6 hours after lowering the pH to 3.4 where as the spectrum at figure 15c was taken only minutes after lowering the pH to 1.8. If allowed to mix for 4-6 hours the colloid at pH 1.8 becomes orange-yellow

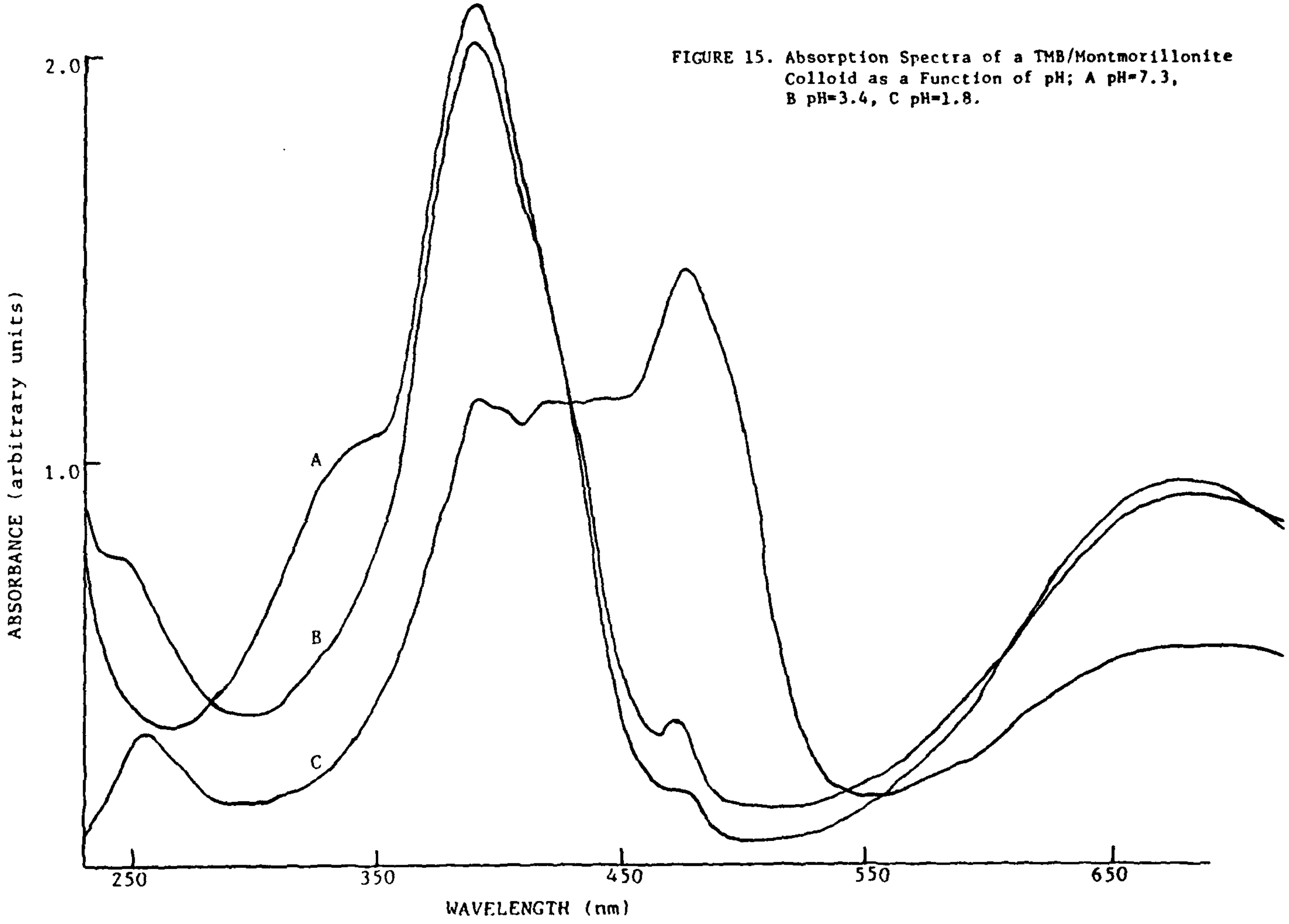


FIGURE 15. Absorption Spectra of a TMB/Montmorillonite Colloid as a Function of pH; A pH=7.3, B pH=3.4, C pH=1.8.

and its absorption spectrum matches the TMB^{2+} reference absorption spectrum, figure 14a. This observation would indicate the unique stability of the TMB^{+} dimer on colloidal clay even in acidic media and would reaffirm that a pH value less than 2.0 is needed for a disproportionation of TMB^{+} dimer to TMB^{2+}.

The growth of the 475 nm absorption peak with lower pH would seem to indicate conclusively the presence of TMB^{2+} on the clay particle surface of a TMB/clay colloid at neutral pH. The presence of an isosbestic point at 430 nm would indicate an equilibrium between the TMB^{+} dimer and TMB^{2+} and is further evidence of the disproportionation reaction at equation 3.

TMB^{+} Dimerization at Low Temperatures and the pH Dependence of the TMB/Montmorillonite Complex 340 nm Absorption Peak

Of the four major absorption peaks or shoulders present in the absorption spectrum of the TMB/clay complex, three have been tentatively identified. The peaks at 340 nm and 680 nm are due to the TMB^{+} dimer while the 475 nm shoulder is caused by the presence of a small amount of TMB^{2+}.

The dimerization of TMB^{+} in low temperature solutions was first proposed by Takemoto, et. al.,[30] who based their calculations on temperature dependent intensity data of TMB^{+}

absorption spectra and demonstrated a value of n=2.0 to 2.3 for the equilibrium:

$$nR^+ \rightleftharpoons Rn^{n+} \qquad (18)$$

The n value equal to 2.0 lead to the conclusion that TMB radical-cations dimerize at low temperatures. However the absorption spectra reported by Takemoto, et al., did not go any lower than 360 nm and it became necessary to repeat their experiment to insure that a TMB^+ dimer in solution did not have an absorption shoulder near 340 nm.

Figure 16 shows the spectrum of TMB^+ monomer formed by the oxidation of $1X10^{-4}$M TMB in ethanol/water by dilute bromine water at room temperature. Figure 16b is the absorption spectrum of the TMB^+ solution lowered to -80 C. The characteristic TMB^+ dimer absorption peaks are present at 390 nm and 680 nm, while the peak at 470 nm indicates the presence of a small amount of TMB^+ monomer. This 470 nm peak disappears completely at -117 C.[30] Figure 16 inset shows the area of interest of the TMB^+ dimer absorption spectrum. No peak or shoulder of any kind is present at 340 nm and it may be concluded that the 340 nm shoulder on the TMB/clay complex is due to the presence of a species other than TMB^+ dimer or TMB^{2+}. The fact that the 340 nm shoulder disappeared on lowering the pH of the TMB/clay complex gives us a clue as to the possible identity of the moiety responsible for this absorption.

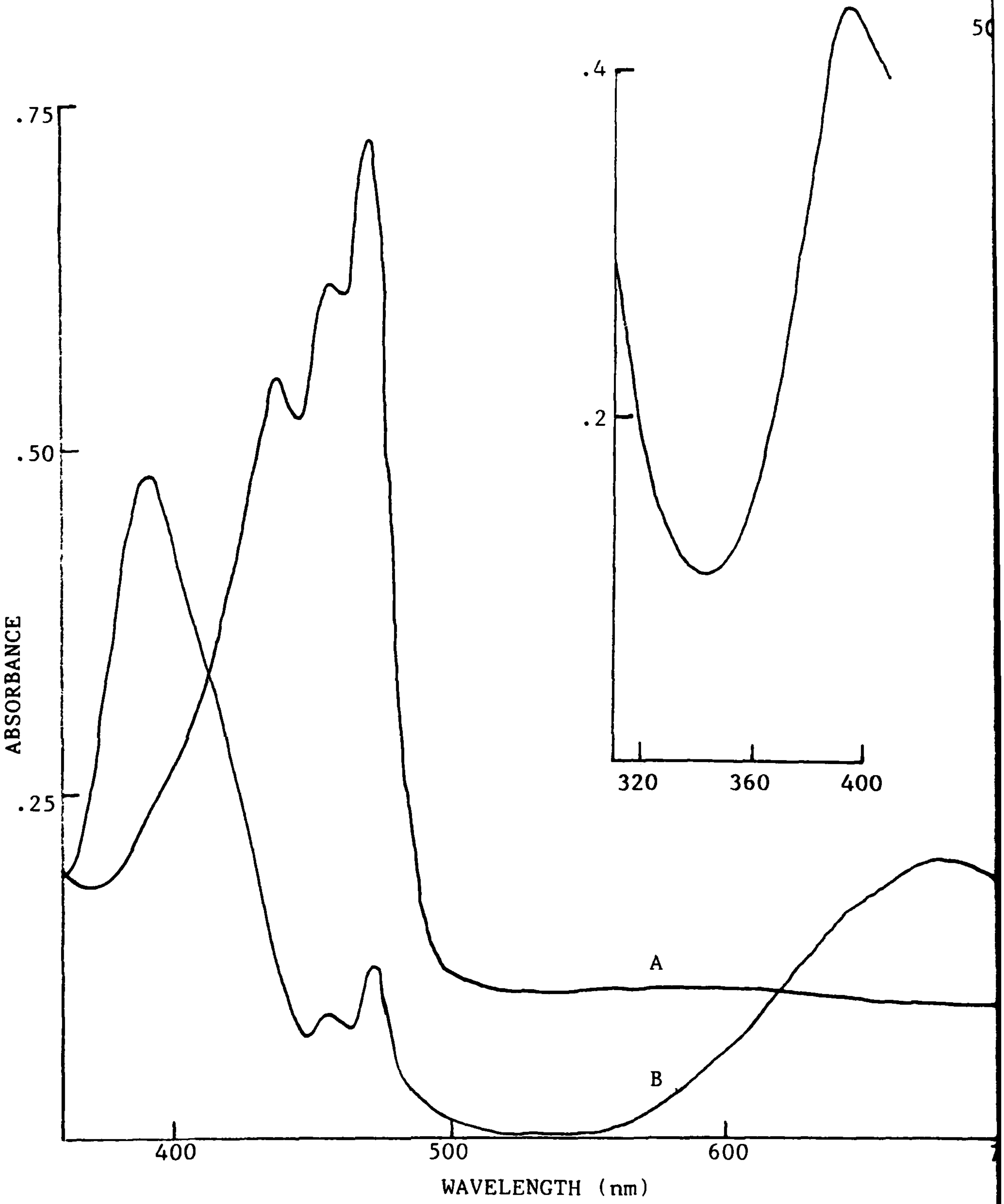


FIGURE 16. Absorption Spectra of TMB^+ in Solution at Room Temperature (A) and at -80°C (B). Inset Highlights Curve B from 320-400nm.

Hausser and Murrell[12] in suggesting dimer formation for organic radicals proposed that radicals can form complexes with diamagnetic molecules as well as with each other. In the case of complexation with a diamagnetic partner the radical could behave as either an electron donor or electron acceptor depending on the nature of its partner.

Dellaguardia[5] has monitored the thermal reaction of TMB with colloidal montmorillonite by means of absorption spectroscopy. He has shown that as the TMB absorption peak (300 nm) decreases and as the TMB^+ dimer (390 nm) absorbance increases an isosbestic point occurs at 340 nm. This indicates an equilibrium between the TMB and TMB^+ dimer during the thermal reaction. It would not seem unreasonable then to propose that as the reaction nears completion TMB^+ might complex with TMB. By lowering the pH the TMB/TMB^+ complex is destroyed as indicated on figure 15b. The two species making up the complex becoming either $TMBH_2^{2+}$ or TMB^{2+} as indicated by increased absorbances at 250 nm and 475 nm respectively.

A TMB/TMB^+ complex is only one possible moiety that could give rise to the 340 nm absorption shoulder of the TMB/clay complex. Since Hausser and Murrell[12] suggested that radical-cations could complex with any diamagnetic partner it is feasible then that TMB^+ could complex with $TMBH^+$ or even TMB^{2+}.

Neutral aromatic TMB is not expected to have any great affinity for montmorillonite. Since the number of cation exchange sites is much greater than the number of TMB molecules TMB would be expected to be intercalated as TMB^+. Therefore the best possible means by which neutral TMB could be intercalated is by complexation with a charged partner.

Electron Paramagnetic Resonance Spectroscopy of TMB and TMPD Adsorbed onto Colloidal Montmorillonite

Absorption spectroscopy experiments have indicated that the adsorption of TMB radical-cations onto colloidal montmorillonite is a very complex reaction resulting in the formation of more than one type of TMB moiety. In neutral solutions the TMB^+ dimer appears to be the dominant species. However there is evidence to suggest the presence of a limited amount of TMB^{2+} as well as a complex formed from the combination of a TMB^+ molecule with a diamagnetic TMB species, most probably TMB or $TMBH^+$.

In an attempt to gain a further understanding of the nature of the TMB/clay complex, electron paramagnetic resonance (EPR) spectroscopy was used to probe the complex.

Figure 17 shows the EPR spectrum of $TMPD^+$ in an ethanol/water solution obtained by oxidizing $1X10^{-4}M$ TMPD with dilute bromine water. The spectrum is characteristic

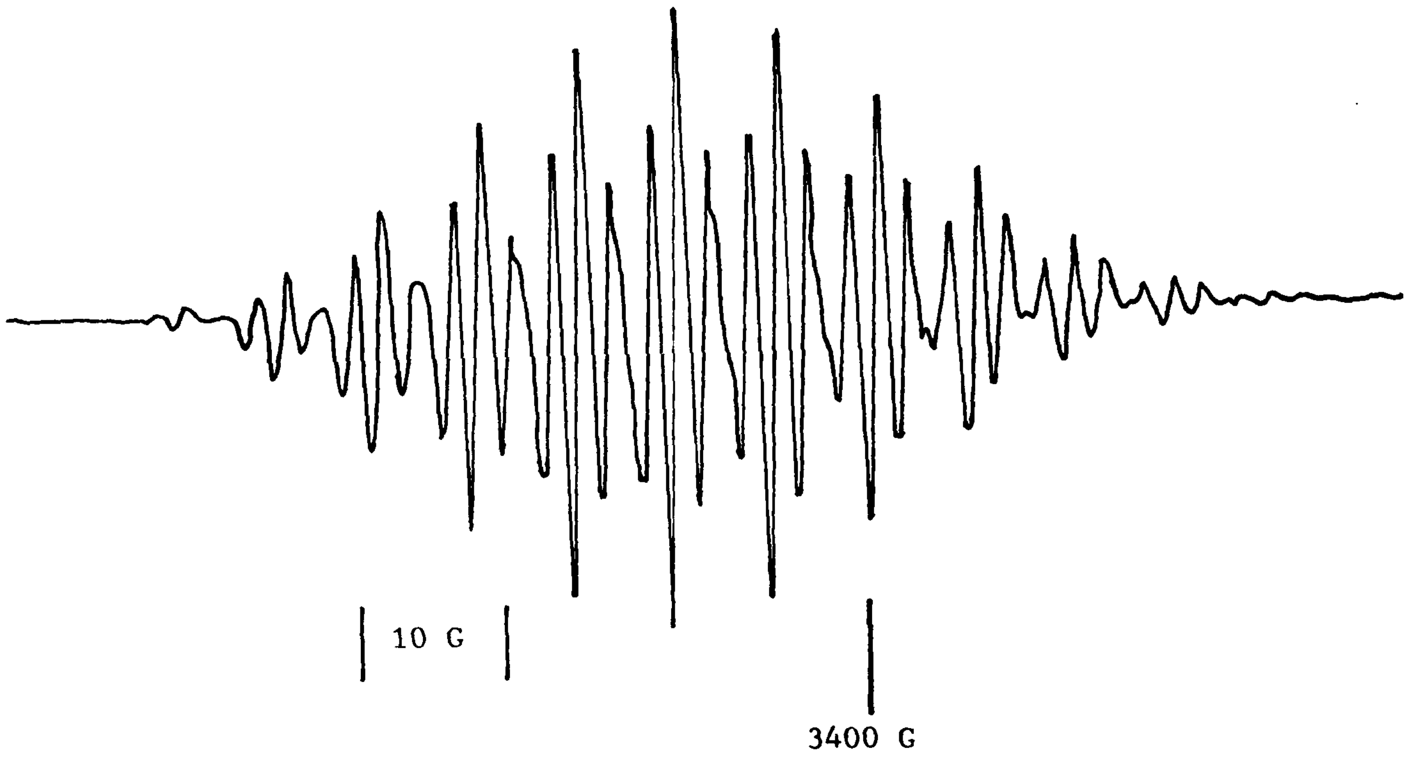


FIGURE 17. EPR Spectrum of $TMPD^+$ in Ethanol/Water Solution at Room Temperature.

of a radical-cation in solution and very closely resembles that of TMB^+ in solution (not shown).

Figure 18 and figure 19 show the EPR spectra of a TMPD/clay complex and a TMB/clay complex respectively. These spectra resemble one another closely and demonstrate the presence of a paramagnetic moiety on the radical-cation/clay complex.

The use of EPR was first considered during attempts to elucidate the nature of the TMB moiety responsible for the yellow color at low pH. If the yellow TMB moiety was in fact the divalent radical-cation, $TMBH^{2+}$, proposed by Theng[31,32] then it would have been expected to give an EPR signal of some kind. However neither the yellow solution formed by the oxidation of $TMBH_2^{2+}$ nor the yellow colloid formed by the reaction of TMB and montmorillonite at pH 1.8 was found to produce an EPR spectrum.

Iida and Matsunaga[15] while probing the nature of solid Wurster salts noticed that some of the salts they were examining exhibited very low magnetic susceptibility. This and the fact that diffuse reflection spectra of these salts resembled neither the monomer or dimer spectrum lead them to propose that in the solids a very strong more-than-by-pairs interaction existed and the salt was considered to be a linear anti-ferromagnet. Iida and Matsunaga proposed that the state with anti-parallel spins was stabilized by charge-transfer

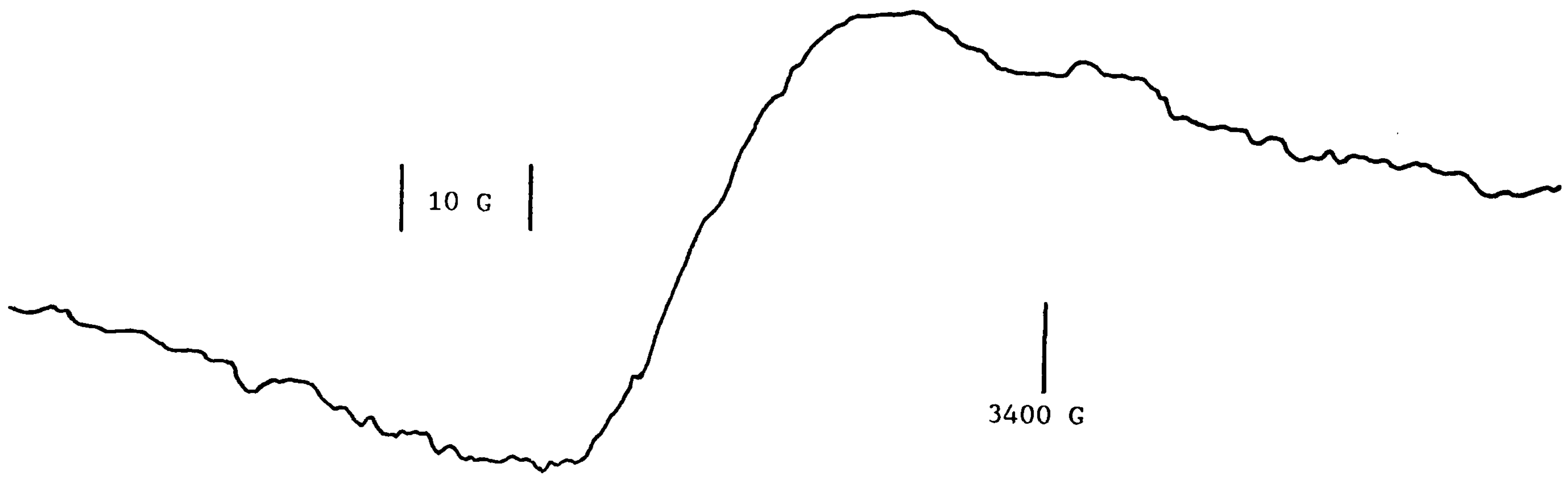


FIGURE 18. EPR Spectrum of 1x10^{-4}M TMPD in Ethanol/Water Solution Complexed with Colloidal Montmorillonite (1 meq/L).

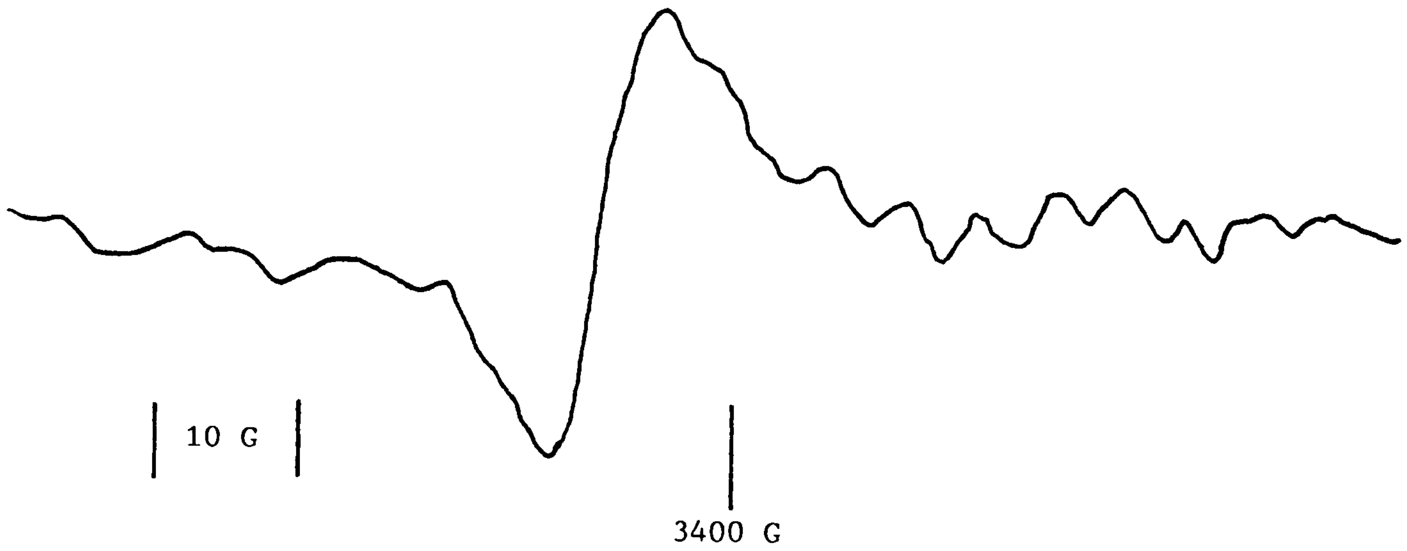


FIGURE 19. EPR Spectrum of 1×10^{-4}M TMB in Ethanol/Water Solution Complexed with Colloidal Montmorillonite (1meq/L).

interactions between various individual radicals. This proposal did not seem plausible when applied to the yellow colored colloidal clay solution. The TMB moiety on the yellow colored clay is a divalent cation and the intermolecular charge repulsion would seem to prohibit close stacking of the cations. The fact that the divalent species would not be expected to closely interact like a monovalent radical-cation would indicate that if the divalent species were a radical-cation some paramagnetism would be exhibited.

Since no paramagnetism was found in the yellow colored colloid, the TMB moiety responsible for the yellow coloring was determined to be TMB^{2+}. This divalent cation would not be expected to exhibit paramagnetism and agrees with absorption data of low pH TMB solutions.

The above information points out that the moiety responsible for the 475 nm absorption shoulder is not responsible for the paramagnetism observed in the green colored colloid. The moiety giving rise to the 340 nm absorption can also be quickly ruled out since the paramagnetism observed in the TMB/clay complex at pH 7.0 is the same at pH 3.4, at which point the 340 nm shoulder is not present.

All this information leads to the conclusion that the paramagnetism observed in the TMB/clay complex is the result of the TMB^+ dimer. It would be thought initially that a dimer constructed from two radical-cations would not exhibit paramagnetism since the spins of the lone electrons on each radical-cation forming the dimer would be anti-parallel.

Thomas, et. al.,[33] proposed that dimers of radical-cations would have a singlet ground state and a triplet excited state. It is possible that on the clay surface the singlet-triplet excitation energy, to which both spin exchange and charge transfer interactions contribute, is substantially lowered. In this case the triplet state of the dimer becomes thermally accessible and paramagnetism may be observed. However the EPR spectra which Thomas et.al., attribute to triplet excitons of excited $TMPD^+$ dimers look nothing at all like the spectra obtained from $TMPD^+$ and TMB^+ on colloidal montmorillonite. These spectra, figure 18 and 19 can best be described as exchange narrowed spectra. This would result from the TMB^+ or $TMPD^+$ molecules being exchange coupled indicating the radicals are close together with a collective interaction extending over many molecules.

This magnetic data, indicating a more-than-by-pairs interaction seems contradictory to spectroscopic data showing primarily by-pairs interaction of monovalent radical-cations.

This contradiction of spectroscopic and magnetic data was also noticed by Uemura, et. al.,[38] during research on the temperature dependence of $TMPD^+$ in the solid phase and in solution. They proposed a model for the interaction of $TMPD^+$ radical cations in which the individual $TMPD^+$ molecules forming the dimer are "loosely bound" and that the electronic states of the radicals are only slightly perturbed by the dimerization. Based on absorption spectroscopy data it would appear that the extent of dimerization of $TMPD^+$ molecules is much greater on colloidal montmorillonite than in low temperature solids. However magnetic susceptibility data would indicate that individual radical-cations are not rigidly held together. The fact that the EPR spectra of TMB^+ and $TMPD^+$ on clay indicates a collective (more-than-by-pairs) interaction may be explained by examining the clay particle surface. If it is assumed that the cation exchange (negative) sites are uniformly distributed over the particle and layer surfaces then the distance separating them would be 8-10Å (appendix 1). This distance would allow sufficient room for dimerization of radical-cations yet would put them in such close proximity to each other that they might interact collectively when exposed to a magnetic field.

Pulsed-Laser Kinetic Study of the TMB Reaction with Colloidal Montmorillonite

It is generally agreed that the uptake of TMB by montmorillonite is primarily (though not simply) a cation exchange process. Pulsed-laser techniques present an ideal method of studying and quantifying the kinetics of the cation exchange process.

Prior to beginning the pulsed-laser kinetic study it was necessary to develop a technique for limiting the thermal reaction of TMB and colloid montmorillonite. Dellaguardia[5] has shown that a significant amount of TMB will react with montmorillonite minutes after the colloid is mixed. To prevent this thermal reaction from interfering with the pulsed-laser experiment a technique was developed that permitted pulsing of a TMB/montmorillonite colloid within 30 seconds after mixing. The thermal reaction of TMB with montmorillonite was determined to be negligible within the 30 seconds prior to the laser pulse and the only TMB^+ molecules on the clay surface after the pulse were those produced in solution by laser photoionization.

Prior to beginning the kinetic study the implicit assumption was made that once a TMB^+ molecule was adsorbed onto the clay surface its nature was changed irreversibly. Therefore by observing the transient decay at 470 nm only the cation exchange process was being monitored. However if the TMB^+ moiety had a long lifetime on the clay surface prior to aggregation or further reaction than the transient decay at 470 nm would be monitoring more than one process. To insure that only a cation exchange process was being monitored it was decided to compare the transient decay at 470 nm to the transient growth at 390 nm since adsorption data indicated that the primary interaction of the TMB^+ molecules on the clay surface is dimeric aggregation.

Figure 20a shows the transient decay of TMB^+ produced by low intensity laser photoionization of $1X10^{-4}M$ TMB in ethanol and water containing .25 meq of montmorillonite. Figure 20b shows the growth of TMB^+ dimer on the same colloid solution. The fact that the half-life of 470 nm decay is very close to the half-life of 390 nm growth indicates that the TMB^+ dimer grows as fast as the TMB^+ monomer decays. This would indicate that the lifetime of the TMB^+ monomer on the clay surface is very short, that movement of TMB^+ monomer on the surface is very fast and that dimerization will take place almost as soon as two TMB^+ monomers are adsorbed onto the same surface. This data would support the implicit assumption made earlier that the cation exchange process can be monitored by monitoring the TMB^+ transient decay at 470 nm.

It was determined very early that the decay of TMB^+ in solution was dependent on the intensity of the laser pulse. As indicated in the experimental section, TMB^+ follows a second order decay process for transients produced by high laser intensity. However by reducing the laser intensity TMB^+ will follow a first order decay process as indicated on figure 21.

The fact that TMB^+ would follow a first order kinetics

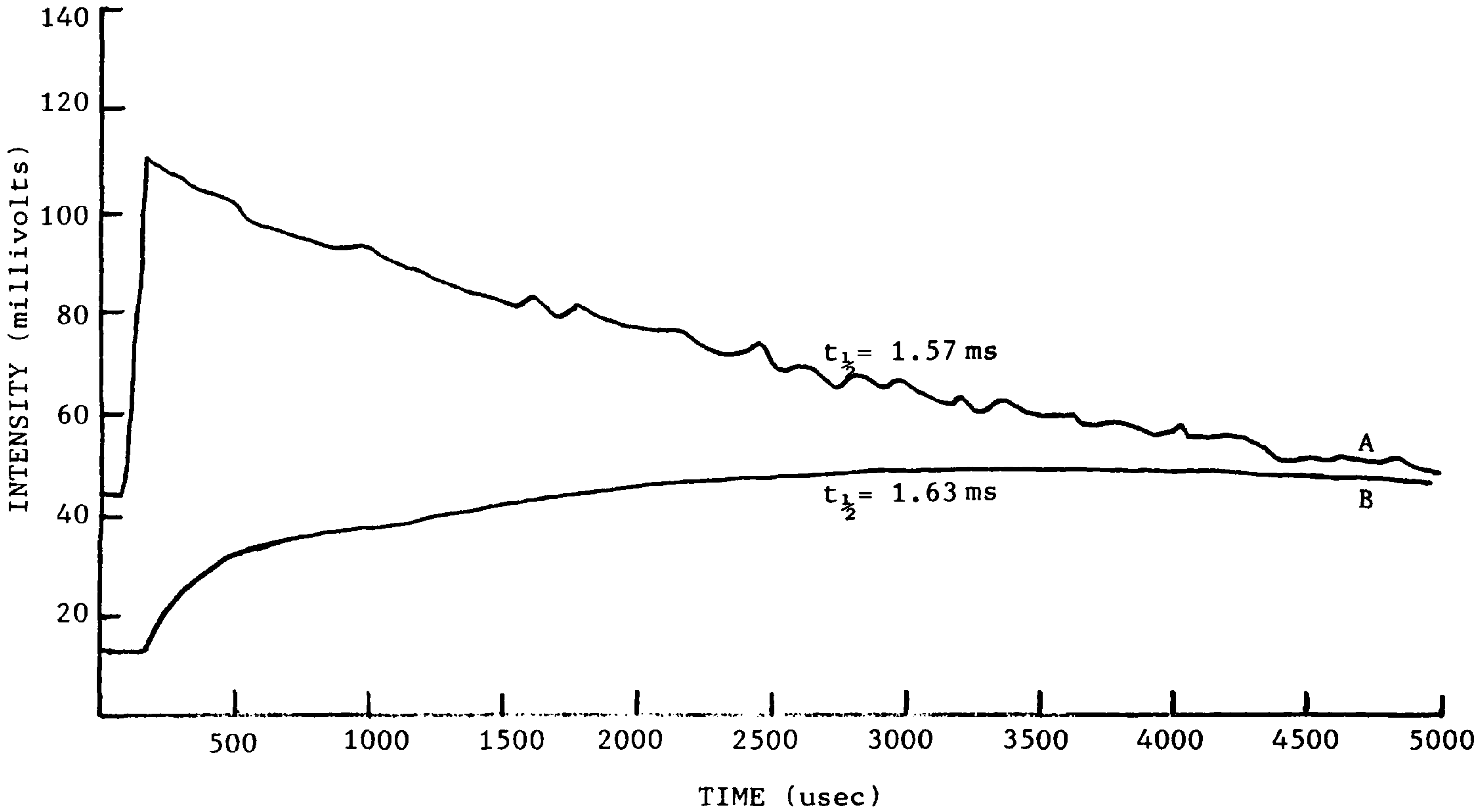


FIGURE 20. Computerized Decay Curve of TMB^{+} in the Presence of Colloidal Montmorillonite (A) and Computerized Growth Curve of $(TMB^{+})_2$ on Colloidal Montmorillonite (B).

Interval # 1 (between 60 & 225)
Rate constant= 3.526E+002
Half-Life (usec)= 1966.04386186
Correlation Coefficient= 0.9856

Interval # 2 (between 75 & 225)
Rate constant= 3.490E+002
Half-Life (usec)= 1986.27497891
Correlation Coefficient= 0.9825

Interval # 3 (between 75 & 200)
Rate constant= 3.877E+002
Half-Life (usec)= 1788.03747466
Correlation Coefficient= 0.9802

1 x 10^{-4}M TMB
H_2O/EtOH (1:1 v/v)

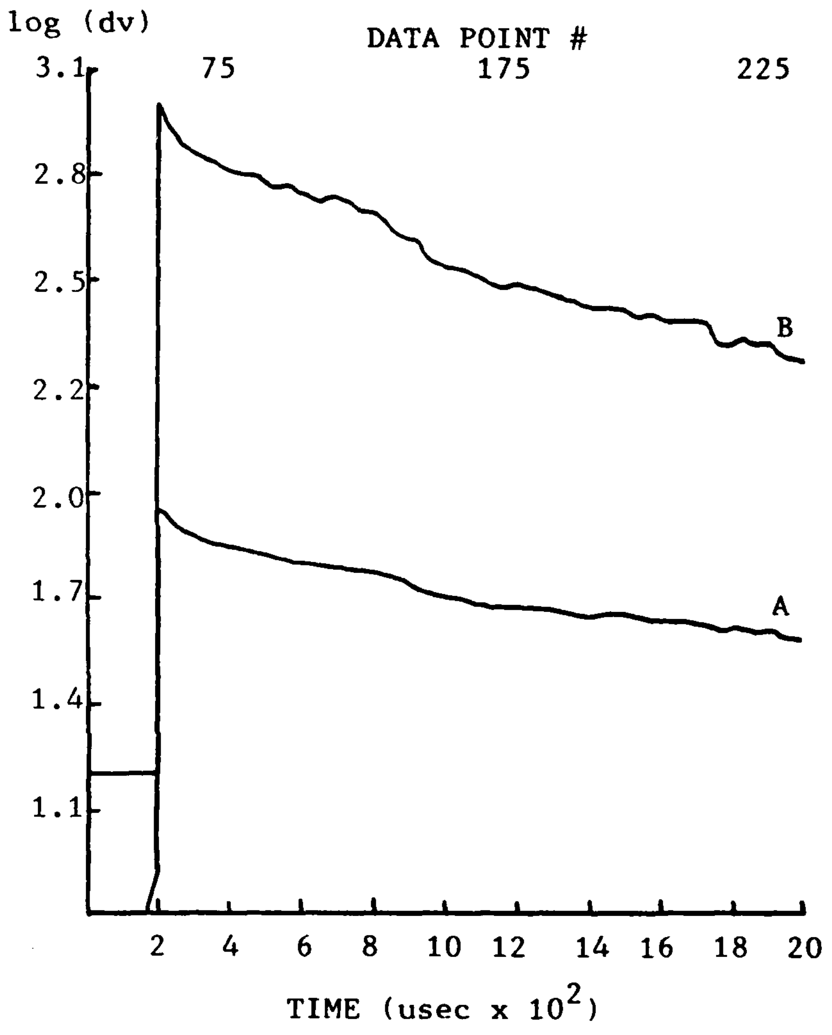


FIGURE 21. Computerized Decay Curve (A) and Log Plot (B) of TMB^+ Produced by Low Intensity Laser Photoionization of 1x10^{-4}M TMB in Ethanol/Water Solution.

allowed the monitoring of the cation exchange process with a Stern-Volmer type of analysis:

$$k = k_o + k_c \,[\text{clay}] \tag{19}$$

where

k = overall rate constant for the decay of TMB^+

k_o = rate constant for the decay of TMB^+ in the absence of clay

k_c = rate constant for the adsorption of TMB^+ onto the clay surface

[clay] = concentration of montmorillonite normally expressed as cation exchange equivalents per liter

A plot of various rate constants, k, determined by the laser and computer assembly described previously versus concentration of montmorillonite will yield a straight line of slope k_c.

Figure 22 shows the plot obtained from the low intensity laser photolysis of $1\text{X}10^{-4}$M TMB in ethanol/water solution at various concentrations of montmorillonite. The solution was aerated to negate TMB triplet formation. The value for k_o was taken from the data on figure 21. The slope from this plot indicates that $k_c = 3.25\text{X}10^6$ L $\text{equiv}^{-1}\text{sec}^{-1}$.

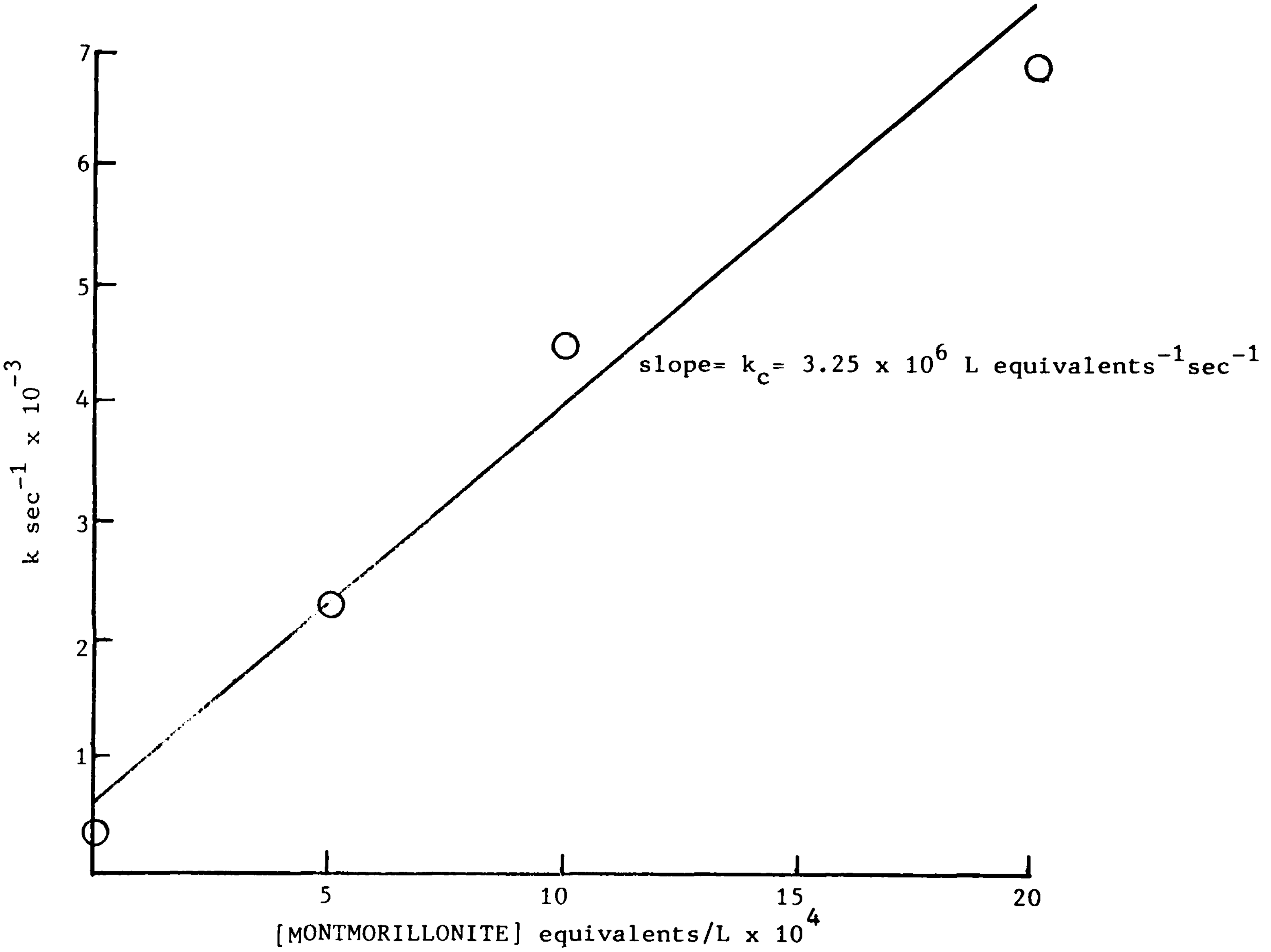


FIGURE 22. Plot of Lifetime Data to Determine the Rate Constant for the Adsorption of TMB^+ onto the Colloidal Montmorillonite Surface.

Solvent Effects on Cation Exchange Kinetics

The kinetics of the cation exchange process of colloidal montmorillonite were studied in SDS micellar solution. Absorption spectroscopy indicates that photolysis of TMB in SDS micellar solution produces the TMB^+ monomer with a spectrum identical to that obtained from chemical oxidation of TMB in polar solvent. Alkaitis and Gratzel[1] have concluded that the SDS is especially stabilized inside the SDS micelles by negative sulfate surface groups. The photoelectron is thermalized in the aqueous phase and prevented from transferring back to TMB^+ by static surface potential.

TMB in SDS micellar solution will react with colloidal montmorillonite in a thermal reaction again demonstrating the unique ability of clays to intercalate organic molecules. However this thermal reaction appears to the eye to be much slower than the reaction of TMB in polar solvents with colloidal clay. This fact can be verified and a quantitative measure can be given through the use of pulsed laser techniques described in the previous section.

TMB^+ transient decay in SDS micellar solution was not expected to be dependent on laser intensity as was TMB^+ in polar solvents. Beck and Brus have shown that TMB^+ ions solvated in SDS micelles cannot approach each other close enough to undergo electron transfer and disproportionation.

This indicates that the bimolecular decay shown at equation 13 is not prevalent in micellar solution. Despite this, low intensity laser light still produced better results and was used so that conditions for TMB/SDS photolysis could be kept similar to those conditions used for TMB photolysis in polar solvents.

Figure 23 shows the transient decay of TMB^+ produced by laser photolysis of $1X10^{-4}M$ TMB in $1X10^{-2}M$ SDS solution. Some transient decay is noticed in the first 50 milliseconds following the laser pulse. This decay is probably due to the presence of small amounts of TMB triplet and non-micelle solvated TMB. The fact that micelles are dynamic structures would indicate that a small portion of TMB would be expected to be in the aqueous phase at any time. However the concentration of micelle solvated TMB is expected to be much greater than that of TMB in the bulk. Therefore analysis of figure 23 indicates no significant decay of micelle solvated TMB^+ in the absence of montmorillonite.

The rate of TMB^+ decay is expected to increase with increasing clay concentration and decrease with increasing SDS concentration.

The rate of TMB^+ decay was measured for a standard solution of $1X10^{-4}M$ TMB and $1X10^{-2}M$ SDS in distilled water with increasing clay concentration. The analysis used was the same as in the previous section, however simplified by

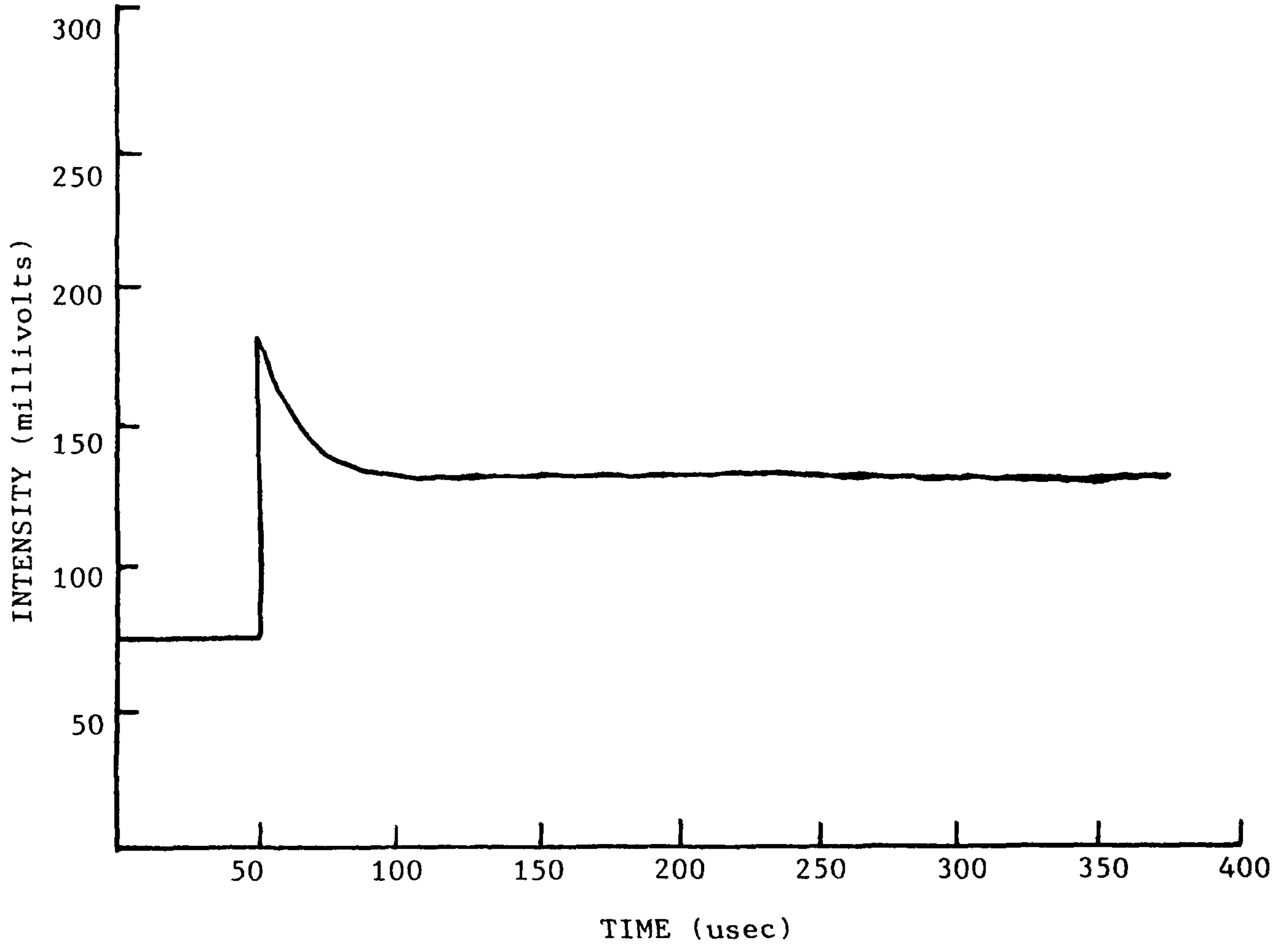


FIGURE 23. Computerized Decay Curve of TMB^+ Produced by Laser Photoionization of $1x10^{-4}M$ TMB in $1x10^{-2}M$ SDS Solution.

the fact that $k_o = 0.0$ since TMB^+ solvated in micelles was not expected to decay and the concentration of non-solvated TMB^+ would be small enough so as not to significantly alter the results.

Figure 24 shows the plot of rate constants, k, for the decay of TMB^+ in $1X10^{-2}M$ SDS at various concentrations of montmorillonite. The plot of k vs. [clay] yields a straight line of slope $k_c = 3.66X10^3$ L $equiv^{-1}$ sec^{-1}. This value indicates that the TMB^+ transient is much longer lived in SDS than in solution, the rate of cation exchange being three orders of magnitude slower than that measured for a polar solvent.

This rate of cation exchange was expected to decrease with increasing SDS concentration. Figure 25 shows the plot of rate constants, k, for the decay of TMB^+ in varying concentrations of SDS. The concentration of montmorillonite was kept constant at 1 meq/L. The slope of the line -44.64 $M^{-1}sec^{-1}$ can only be used as a qualitative measure. The negative slope indicates that increasing the concentration of SDS will significantly alter the TMB^+ transient decay and therefore the rate of cation exchange at the montmorillonite surface.

Attempts to measure the rate of decay of TMB^+ in .1M SDS with varying concentration of clay proved unsuccessful since the lifetime of the TMB^+ transient decay was so long

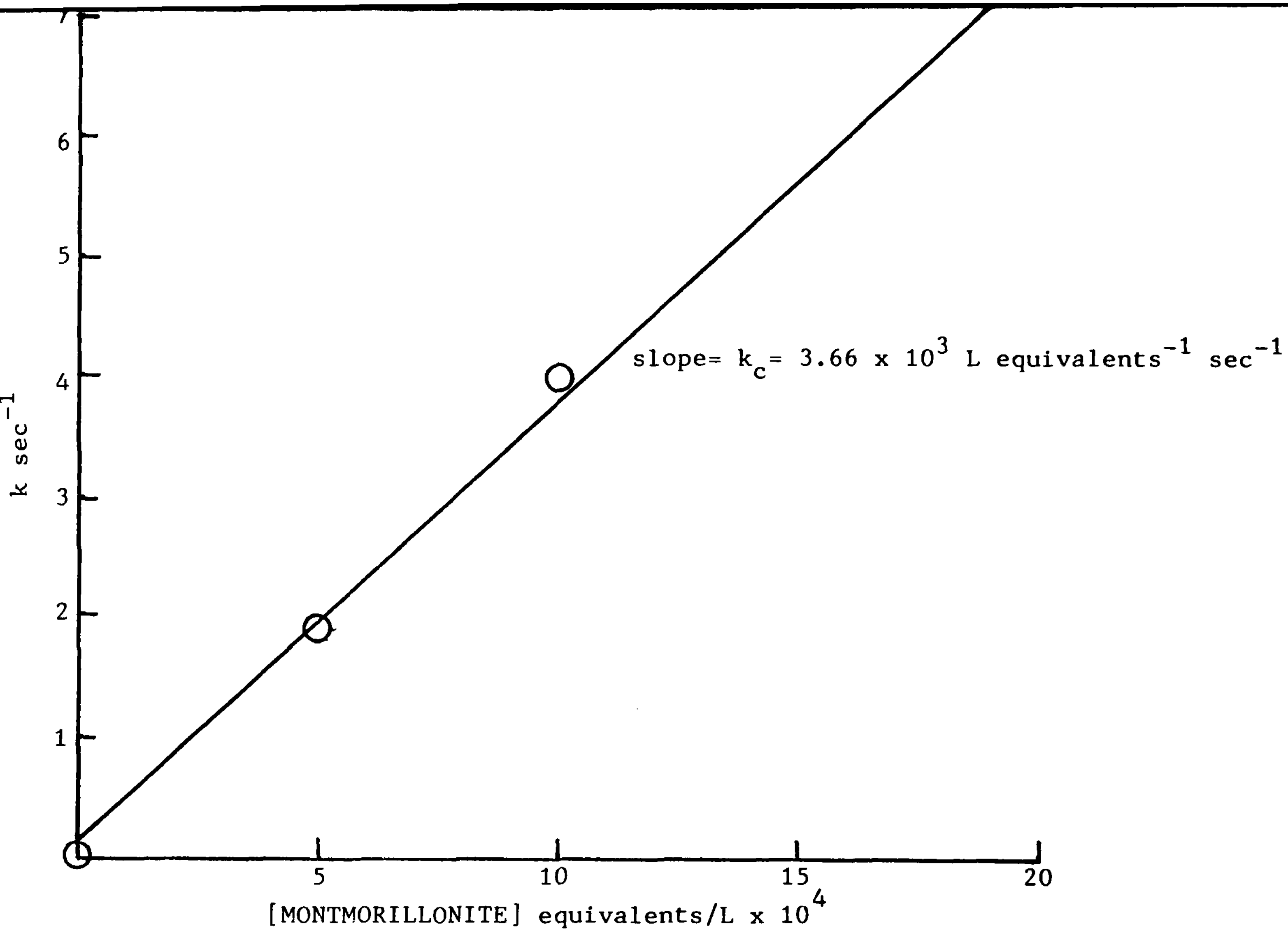


FIGURE 24. Plot of Lifetime Data to Determine Rate Constant for the Adsorption of TMB^+ onto the Colloidal Montmorillonite Surface in the Presence of $1x10^{-2}M$ SDS.

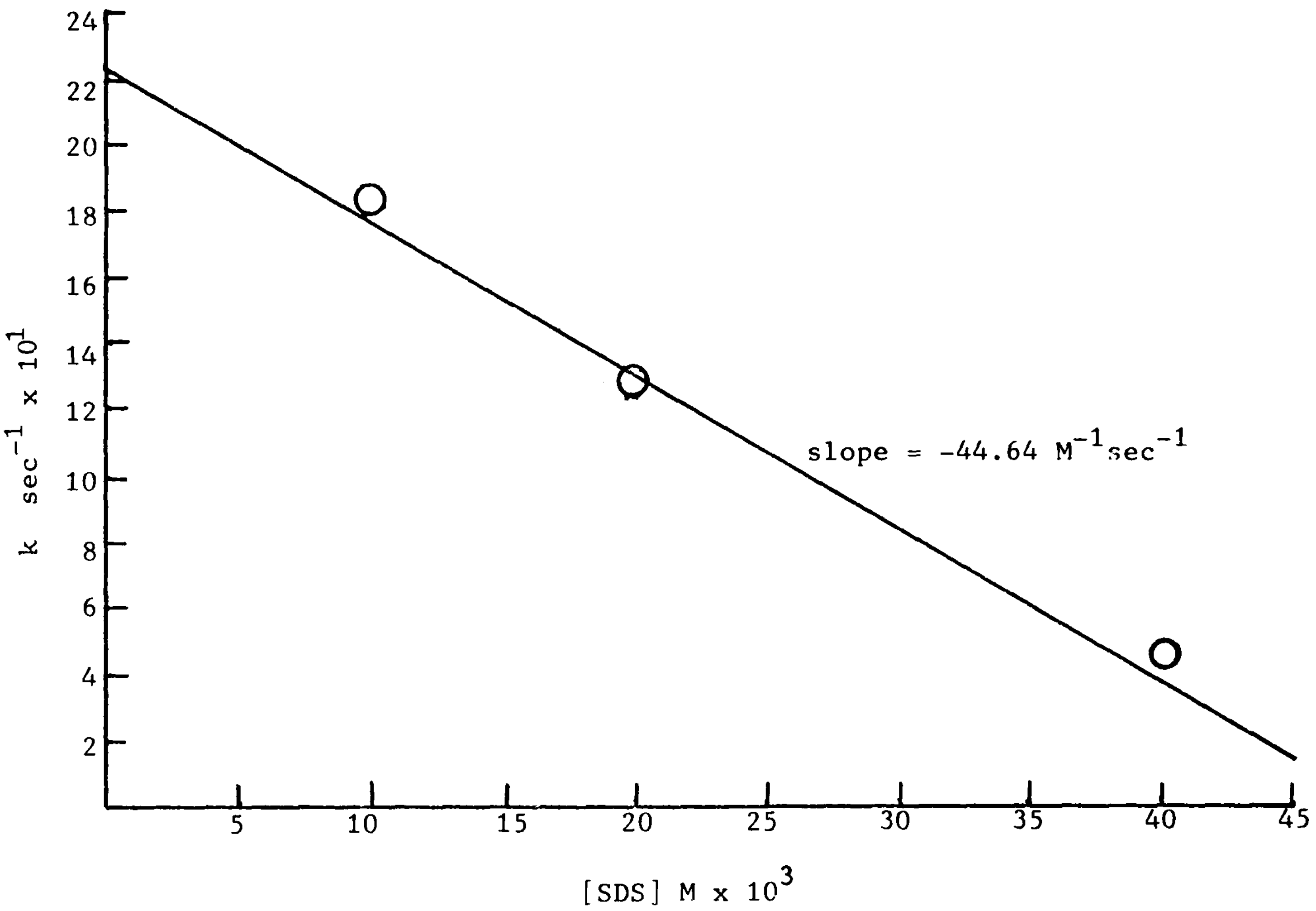


FIGURE 25. Plot of TMB^+ Lifetime Data Demonstrating the Effect of Changing SDS Concentration in the Presence of 1meq/L Montmorillonite.

it was beyond the capacity of the instruments to measure it.

Since the plot at figure 25 is a linear relationship it may prove useful in determining the extent to which TMB^+ is solvated in the SDS micelles. Due to the fact that the micelle is a dynamic structure and that TMB^+ can only be adsorbed on the clay surface if it is outside of the micelle in the aqueous bulk then the following equilibrium can be proposed:

$$TMB^+ + SDS \rightleftharpoons TMB^+/SDS \qquad (20)$$

Under most circumstances the equilibrium would be far to the right. A relative percentage of TMB^+ not solvated in the micelles could be determined by examining the rates of TMB^+ decay in solution ($ETOH:H_2O$) vs SDS. The rate for the decay of TMB^+ in solution with 1 meq of montmorillonite is $k = 4.485X10^3 \text{ sec}^{-1}$ and for $1X10^{-2}M$ SDS with 1 meq clay is $k = 1.808 \text{ sec}^{-1}$. A ratio of these two values:

$$\frac{k_{micelle}}{k_{solution}} = 4.031X10^{-4} \qquad (21)$$

indicates that only four one-hundreths of a percent of TMB^+ ions produced by the laser pulse are in the aqueous bulk following photoionization. This limited availability of TMB^+ ions further explains the reduced rate determined for cation exchange between a micelle and a clay colloid particle.

The Effect of Clay Particle Size on Cation Exchange Kinetics

In addition to solvent affecting the cation exchange rate, the size of the clay colloid particle was thought to play a critical role. Larger particles would have less surface area available for cation exchange and a slower rate would be observed than that determined for smaller colloid particles.

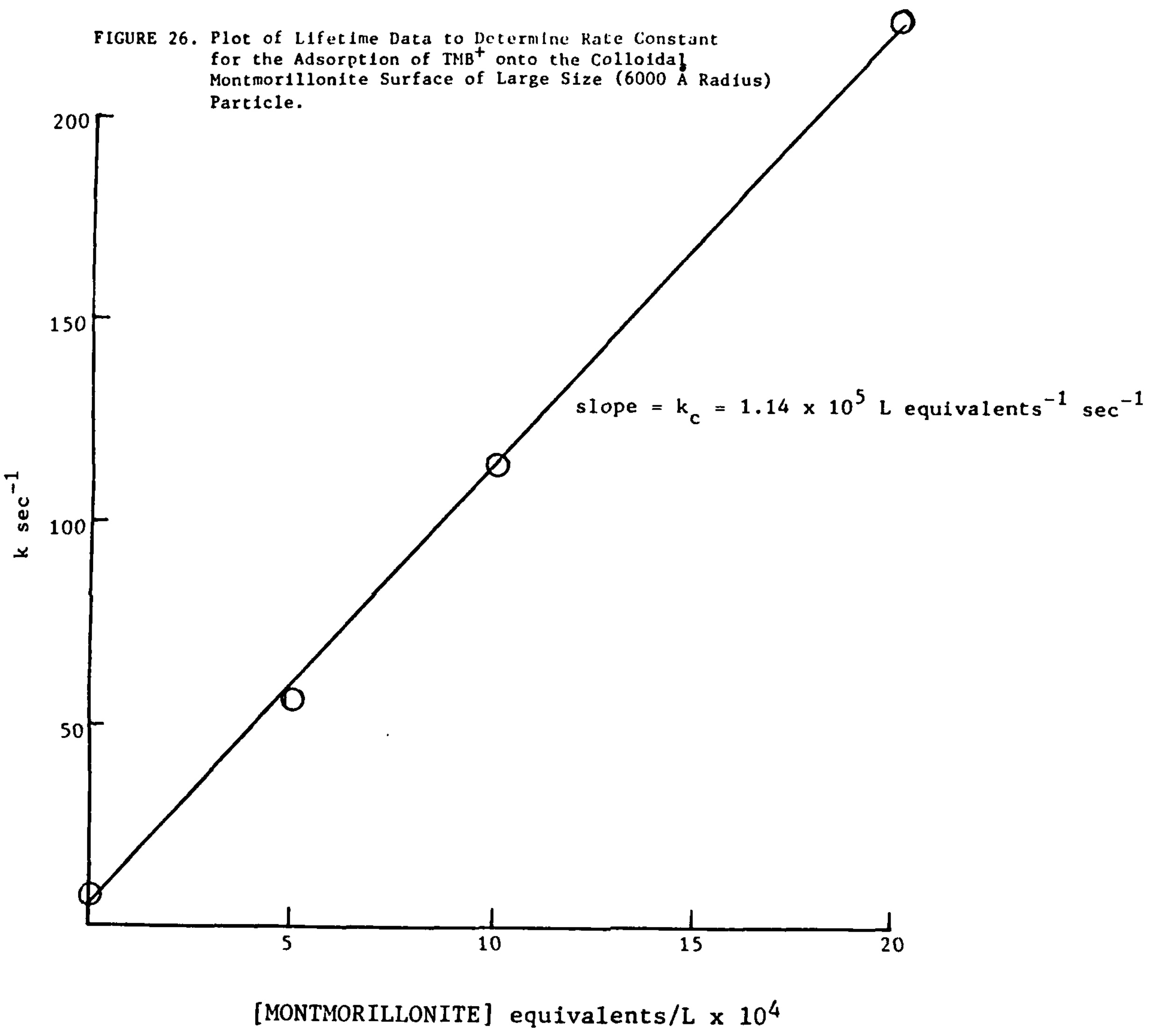
The normal particle size for the montmorillonite colloid used in this study was on the order of 1500-2000Å radius. A colloid was prepared with a particle size of 6000-6300Å radius. This colloid was very turbid and was not nearly as transparent in the visible as the normal colloid.

The analysis of the rate constant obtained at various concentrations of the large particle size clay indicated a significant change in the cation exchange rate constant, k_c.

A plot of rate constant obtained for the decay of TMB^+ in ethanol/water solutions at varying concentrations of the 6000Å particle size clay is shown at figure 26. The value for $k_c=1.137X10^5L\ equiv^{-1}sec^{-1}$ indicated a significant decrease in the rate at which TMB^+ is adsorbed on the montmorillonite surface with the increased particle size.

To determine if a generalized statement could be made

FIGURE 26. Plot of Lifetime Data to Determine Rate Constant for the Adsorption of TMB^+ onto the Colloidal Montmorillonite Surface of Large Size (6000 Å Radius) Particle.



concerning the effect of particle size on the cation exchange rate a colloid was prepared with an average particle radius of 4000Å. This colloid produced a cation adsorption constant, $k_c=5.13X10^5$L equiv^{-1}sec^{-1}. These values for the exchange constants for increased particle size compared to the base value for the 1500-2000Å radius colloid $k_c=3.25X10^6$L equiv^{-1}sec^{-1}, produce a general relationship that the rate varies as $1/r^3$, where r is the ratio of the radius of the larger particle size to the standard particle radius (1500-2000Å).

CHAPTER IV

CONCLUSION

It is an established fact that clay minerals in the soil will detoxify adsorbed pesticides. It is this ability of clay minerals to adsorb toxic organic molecules and catalyze their decomposition which has spurred recent research on the reaction of organic material with clay minerals[3,4] and clay mineral analogues[40]. The use of photochemical techniques to probe the nature of the reaction of the organic moiety with the clay mineral and the resulting organo/clay complex was proposed to be an ideal method for a number of reasons. First, recent advances in the laser flash photolysis techniques allow studies of the movement of excited species from the bulk solution to the clay particle as well as provide information on the nature of the molecule once it is adsorbed on the clay surface. Secondly much work has been done in recent years utilizing organic colloidal aggregated structures to promote both thermal and radiation induced reactions and it is appropriate to extend this work to inorganic systems such as clay colloids. Lastly and probably most importantly, the use of photochemistrv to probe the organo/clay complex can simulate actual conditions in nature where molecules adsorbed on clays are being photolyzed by sunlight.

In addition to detoxifying pesticides, the unique nature of clay minerals permits them to catalyze many chemical reactions. Most of these reactions are catalyzed by clays which are "activated" by either drying them to the point that most of their interlayer water is evaporated or by boiling them in strong acids and then drying them. In either case the resulting catalytic activity results from the increased proton donating ability (Bronsted acidity) of the clay mineral. Even without "activation" many clay minerals will demonstrate reactivity due to the presence of reactive sites on the mineral surface. These sites are the result of Al atoms on the crystal edges which act as Lewis acid sites as well as Redox sites resulting from isomorphous substitution of transition metals for the two primary inorganic building atoms of clay minerals, Si and Al.

Of the many clay minerals available for study, montmorillonite was the mineral of choice for this work. Montmorillonite has the most unique adsorption power for organic materials due primarily to the ability of its layers to expand and intercalate charged or ionic species and also due to its high CEC.

In addition to its unique adsorption power for organic material montmorillonite could produce colloidal particles in the order of 1500Å radius. This small particle size offers many advantages to the photochemist. It can produce a colloidal solution that is only slightly turbid to the eye and is practically transparent in the visible and near

UV. The small size of the particle can increase the catalytic efficiency of the mineral and this coupled with the high CEC of montmorillonite permitted the use of small quantities of organic material with small quantities of clay to initiate high yield reactions. Also the small particle size allowed the use of laser flash photolysis techniques to study the cation exchange process and adsorption of organic ions onto the clay surface.

In addition to being nearly transparent in the visible, the clay colloid offered the advantage of being fully hydrated. As indicated earlier, the presence of water in the layers of clay often hindered its reactivity. However hydrated colloidal clays permit study of organo/clay reactions with the hope that certain of these reactions will be promoted in the presence of water. This is a desirable feature since clay used on a commercial scale for toxic waste decontamination would probably be mixed with water and sprayed as a colloid or slurry.

This work re-examines a classic clay-organic reaction. That is the reaction of an aromatic amine, TMB, with montmorillonite to form its colored derivatives, TMB^{+} and TMB^{++}. Although this reaction is considered classic and has been widely studied it was thought that the use of colloidal clays would produce color reaction which could be easily studied by solution photochemical techniques. This would offer many advantages over past techniques which depended on qualitative color changes and/or diffuse reflection spectra of dried or nearly dry clay samples. This reliance on spectra from dried clay samples often was unable to account for the changing reactivity of the clay during the drying process. It was also felt that new information on the reaction of TMB in solution and in micelles might assist in the interpretation of data obtained from reactions occuring in colloidal solution.

Absorption data of a TMB^+/montmorillonite colloidal solution indicates that the TMB^+ tended to aggregate and that the primary mode of aggregation is dimeric. It seems that montmorillonite has the ability to sequester or colonize adsorbed organic cations. This would appear to be due to the fact that these TMB^+ ions are forced to be adsorbed on the negatively charged particle surface but have no affinity for the inorganic material there, hence they tend to cluster together. The dimerization of TMB^+ molecules results from a proximity effect or an increased local concentration due to their clustering. This dimerization of monovalent radical-cations of aromatic amines was confirmed by spectroscopic data on $TMPD^+$ and MV^+ adsorbed on colloidal montmorillonite.

Perhaps more intriguing than the dimerization of TMB^+ on clay was the presence of more than one type of TMB moiety on the clay surface. Spectroscopic data indicates that these species are probably TMB^{2+} and a complex formed from a TMB^+ monomer with a diamagnetic partner, probably TMB or $TMBH^+$. Evidence for this complex is limited and it may be argued that the species is just unreacted TMB on the clay surface. However, TMB has a limited affinity for the clay surface and would best be intercalated by complexation with TMB^+. In all studies the number of cation exchange sites far outnumbered the number of TMB molecules and it can be argued that the only way a TMB molecule could exist in its neutral form without reacting would be as a complex.

Though the green color on a TMB/clay colloid has been ascribed to the dimerization of TMB^+ ions the species responsible for the yellow color at low pH could not be attributed to the aggregation of TMB^+ ions. As late as 1974 the yellow species of TMB was thought to be the protonated form of the monovalent radical cation, $TMBH^{2+}$. However recent data on the reaction of TMB^+ in acidic media indicates a disproportionation reaction, producing TMB^{2+}, $TMBH_2{}^{2+}$ and the yellow color. This reaction is not unreasonable for the reaction of TMB on montmorillonite at low pH and coupled with the fact that the yellow clay colloid does not have an EPR spectrum leads to the conclusion that the primary species on the clay surface responsible for a yellow color is the divalent cation, TMB^{2+}, and not the divalent radical cation, $TMBH^{2+}$.

EPR data on the divalent cation on clay proved non-existent but an EPR spectrum produced by the green colored colloid was very interesting. This spectrum showed a collective interaction of TMB^+ monomers, contrary to absorption data. However if it is assumed that TMB^+ monomers are located at negative sites on the clay surface 8-10A apart then this distance may produce a "loosely bound" dimer which gives spectroscopic data indicative of dimerization but permits magnetic interaction between dimers and over many molecules (TMB^+ monomers).

Laser flash photolysis techniques were employed to monitor the rate at which cations are adsorbed onto the clay surface. Previous works had indicated that the primary reactions of clays with organic molecules such as TMB is cation exchange. The use of low intensity 308 nm laser light to photoionize TMB and a computer assembly to monitor the decay of TMB^+ at 470 nm permitted a measure of the cation exchange process. The TMB^+ ions are adsorbed onto colloidal montmorillonite at a rate constant,

$$k_c = 3.25 \text{X} 10^6 \text{ L equivalents}^{-1} \text{ sec}^{-1} \qquad (22)$$

This process can be affected by both changing the solvent and increasing the particle size. In both cases a decrease in the rate constant was observed.

This work does not pretend to be complete. Much research is needed to elucidate all the processes involved in the color reaction of aromatic amines with montmorillonite colloids. However some information has been uncovered and some techniques developed during the course of this research which help shed some light on the important interfacial processes at the clay surface. The encapsulating of organic material in an uniquely inorganic environment such as clay minerals is sure to spur additional research and only then will the nature of the many processes be understood.

APPENDIX I

SELECTED CALCULATIONS FOR A MONTMORILLONITE COLLOID

Montmorillonite clay forms particles in solution known as tactoids, or plate-like as depicted in figure 27. The composition of the plates, or layers, has been described previously. For a montmorillonite colloid with Na^+ as the primary counterion, the particles will consist of 3 or 4 layers. The optimum particle size has been determined to be 1500 - 2000Å radius. The calculations described in this section are for an average, fully hydrated particle. This means 3 layers of dimensions 4000Å x 4000Å x 70Å. The interlayer spacing is 20Å due to the sorption of the maximum amount of water allowed. The density of a fully hydrated montmorillonite clay is 1.56 g/cm^3.[9]

1. <u>Surface area of a particle.</u>

$$\text{Outside} = (4)(70\text{Å})(4000\text{Å}) + (2)(4000\text{Å})(4000\text{Å}) = 33.12\text{x}10^6\text{Å}^2$$

$$\text{Inside} = (4)(4000\text{Å})(4000\text{Å}) = 64.00\text{x}10^6\text{Å}^2$$

$$\text{Total} = \text{Inside} + \text{Outside} = 97.12\text{x}10^6\text{Å}^2/\text{particle}$$
$$= 9.71\text{x}10^{-13}\text{m}^2/\text{particle}$$

2. <u>Total volume of a particle.</u>

$$\text{Volume} = (70\text{Å})(4000\text{Å})(4000\text{Å}) = 1.12\text{x}10^9\text{Å}^3/\text{particle}$$
$$= 1.12\text{x}10^{-21}\text{m}^3/\text{particle}$$
$$= 1.12\text{x}10^{-15}\text{cm}^3/\text{particle}$$

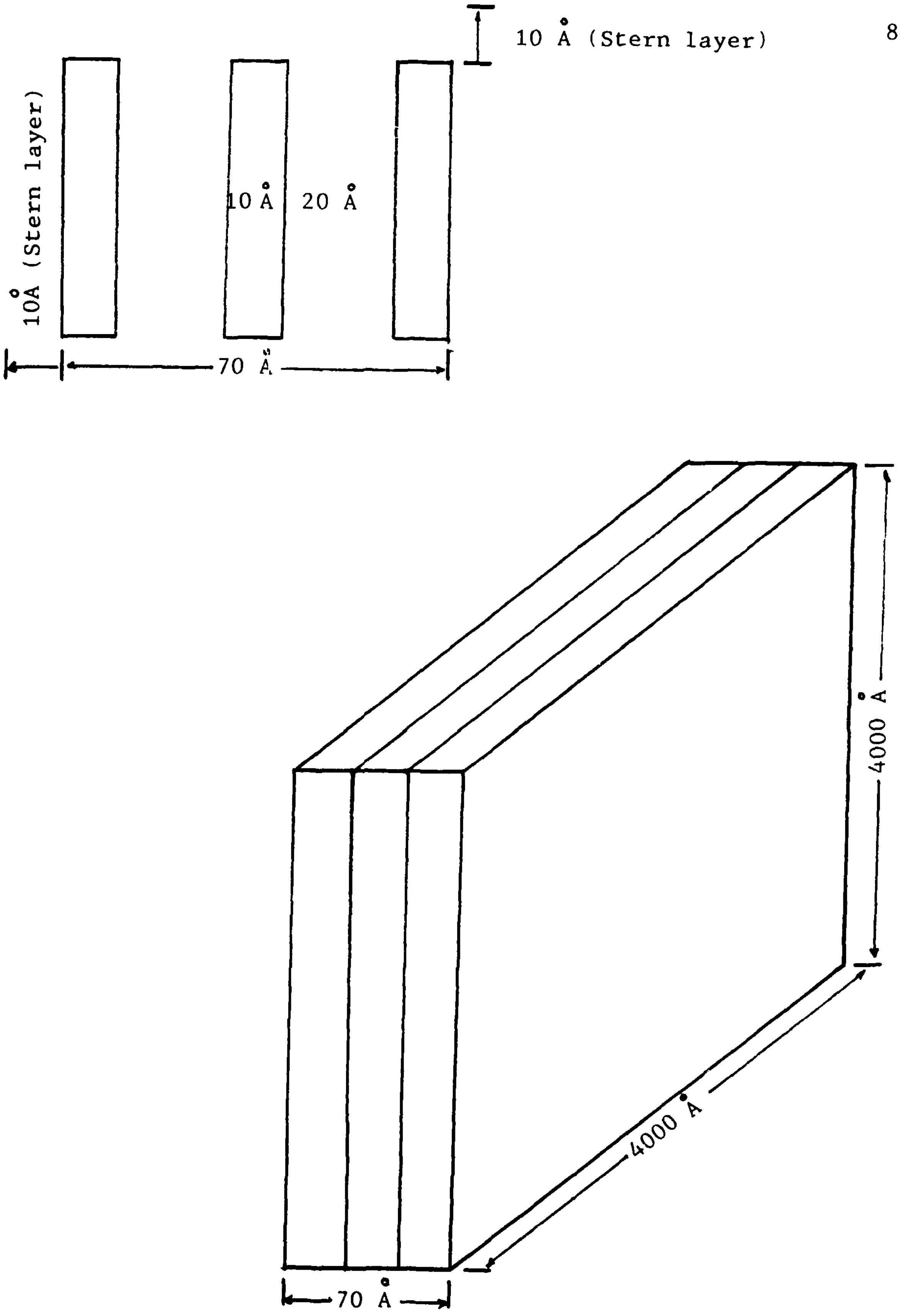


FIGURE 27. Diagram of Typical Montmorillonite Colloid Particle.

3. Total particles for a standard colloidal solution (1 g/L).

$$\text{Total} = (1.56\ \text{g/cm}^3)(1.12\text{x}10^{-15}\ \text{cm}^3\text{/particle})$$
$$= 1.75\text{x}10^{-15}\ \text{g/particle}$$
$$= 5.71\text{x}10^{14}\ \text{particles/g}$$
$$= 5.71\text{x}10^{14}\ \text{particles/L}$$

4. Cation exchange sites per particle.

$$\#\ \text{Sites} = (1.75\text{x}10^{-15}\ \text{g/particle})(1\text{x}10^{-3}\text{equivalents/g})$$
$$(6.02\text{x}10^{23}\ \text{charges/equivalent})$$
$$= 1.05\text{x}10^{6}\ \text{charges/particle}$$
$$= 1.05\text{x}10^{6}\ \text{sites/particle}$$

5. Distance separating exchange sites(charges) by surface area.

$$\text{Distance} = ((97.12\text{x}10^{6}\text{Å/particle})(1.05\text{x}10^{6}\text{charges/particle}$$
$$= (92.49\ \text{Å}^2\text{/charge})^{\frac{1}{2}}$$
$$= 9.62\text{Å/charge}$$

6. Total montmorillonite surface area for a standard colloidal solution (1 g/L).

$$\text{SA} = (9.71\text{x}10^{-13}\text{m}^2\text{/particle})(5.71\text{x}10^{14}\text{particles/g})$$
$$= 5.54\text{x}10^{2}\text{m}^2\text{/g}$$
$$= 5.54\text{x}10^{2}\ \text{m}^2\text{/L}$$

7. Total montmorillonite volume for a standard colloidal solution.

$$\text{V} = (1.12\text{x}10^{-21}\text{m}^3\text{/particle})(5.71\text{x}10^{14}\text{particles/g})$$
$$= 6.39\text{x}10^{-7}\ \text{m}^3\text{/g}$$
$$= 6.39\text{x}10^{-1}\ \text{cm}^3\text{/g}$$

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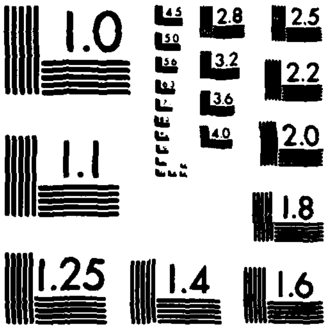

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APPENDIX II

LOCAL EFFECTIVE CONCENTRATION

Due to the adsorption of molecules on the montmorillonite particles the effective concentration of TMB^+ or other adsorbed organic molecules is much greater than the bulk solution concentration. When determining a value for effective local concentration it is inappropriate to use the volume of a particle determined in Appendix I. The most correct method involves determining the volume for intercalation of organic molecules. The surface volume and internal volume for intercalation of the montmorillonite colloid are calculated from the width of the Stern layer on the outside of the particle (10Å), the interlayer spacing distance (20Å), the length of the particle along its edge (4000Å), the thickness of an alumino-silicate sheet (10Å), and the number of montmorillonite particles in solution.

1. <u>Volume for intercalation.</u>

Internal Volume= $(2)(20\text{Å})(4000\text{Å})^2 = 6.40\text{x}10^8\ \text{Å}^3/\text{part.}$

External Volume= $(2)(10\text{Å})(4000\text{Å})^2 + (6)(10\text{Å})^2(4000\text{Å})$

$= 3.22\text{x}10^8\ \text{Å}^3/\text{particle}$

Total Volume= $9.62\text{x}10^8\ \text{Å}^3/\text{particle}$

$= (9.62\text{x}10^8\ \text{Å}^3/\text{particle})(5.71\text{x}10^{14}\text{part/g})$

$(1\text{x}10^{-24}\ \text{cm}^3/\text{Å}^3)$

$= 5.50\text{x}10^{-1}\ \text{cm}^3/\text{g}$

2. Effective local concentration.

Assume standard colloidal solution, 1 g/L, and bulk solution concentration of 1×10^{-4}M. Use knowledge of spectroscopic data indicating all ionic species are intercalated into the clay.

concentration= $(1\times10^{-4}\text{moles})/((5.50\times10^{-1}\ \text{cm}^3/\text{g})$
$(1\ \text{g})(1\times10^{-3}\ \text{L}/\text{cm}^3))$
$= 1.82\times10^{-1}$ M

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