This is to certify that the

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IN SMECTITES

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By

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ABSTRACT

ON THE INTERCALATION OF ORGANOSILICON COMPOUNDS IN SMECTITES

By

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Smectites inherently possess many of the properties desirable in a catalyst support or molecular sieve. Some of their shortcomings may be removed by processes which result in the intercalation of silica props. The preparation of thermally stable pillared smectites utilizing intercalated silica has been reported. The product is achieved via adsorption and subsequent interlayer modification of the tris(acetylacetonato)silicon(IV) cation. An organosilicon intercalate is therefore a precursor to this method of silica intercalation.

The elucidation of this mechanism of organosilicon intercalation was a major goal of this research. The interaction of smectites with phenyltrichlorosilane was investigated as an alternative organosilicon intercalate.

Interactions of tris(acetylacetonato)silicon(IV) with homoionic smectites were studied in water and acetone, and subsequent counterion desorption determined. Hydrolysis of the organosilicon complex cation, free in water, was found to proceed as a temperature dependent pseudo-first order process with a half-life on the order of hours. Hydrolysis of the organosilicon complex cation residing at the clay surface was found to be diffusion controlled with a half-life on the order of weeks. Traditional adsorption isotherms for this system cannot be reported due to the time dependent nature of complex cation (adsorbate) concentration. Another method for treating this information is described. Temperature, solvent systems, and specific counterion were found to be the most important factors affecting the rate, completeness, and mechanism of tris(acetylacetonato)silicon(IV) adsorption by smectites.

The phenyltrichlorosilane system was amenable to traditional adsorption isotherm treatment. The affinities of the smectites for phenyltrichlorosilane are reported, as their counterions, in increasing order: Na < Mg < Co < Cu. The silane apparently does not produce a thermally stable pillared intercalate, since all clays studied had collapsed by 300C.

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The verb, appreciate, may be used to indicate high esteem, or to denote an increase in value over time. Both meanings are intended here.

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TABLE OF CONTENTS

PAGE

LIST OF TABLES

TABLE PAGE

PART I

PART II

LIST OF FIGURES

FIGURE PAGE

PART I

LIST OF FIGURES -- Continued

FIGURE PAGE

PART II

INTRODUCTION

The layer lattice silicates known as smectites are a ubiquitous group of clay minerals possessing mica-like structures. Smectites are composed of units having two silica tetrahedral sheets that "sandwich" a central alumina octahedral sheet. The (001) "tips" of the tetrahedrons all point toward the center of the unit. The tetrahedral and octahedral sheets are juxtaposed so that the (001) apices of the tetrahedra, and one of the hydroxyl layers of the octahedra, reside in a common plane. Oxygen atoms are "shared" by both the tetrahedral and octahedral layers, unlike the hydroxide groups which are solely octahedral apices. All layers are continuous in the a and b directions and are stacked, one above the other, in the c direction (Grim, 1968).

Individual members of the smectite group arise from the variety and degree of isomorphous substitution of metal cations at the centers of the polyhedra of the mica model. Tetravalent silicon (Si) may be replaced by trivalent aluminum (Al) in the tetrahedral layers. Trivalent Al may be replaced by divalent magnesium (Mg) and/or iron (Fe) in the octahedral layer. Other substitutions are less common but all result in a deficit of positive charge, since lower valence cations occupy lattice sites which in the mica model are charge balanced only for the higher valence cations. Charge deficit may arise due to substitution in both types of layers.

The charge deficit on these colloid sized particles is brought to zero by the adsorption of appropriate numbers of hydrated cations. Both the external and interlayer surfaces of these particles provide sites for cation exchange but it is the chemistry of the interlayer volume that gives smectites their shrink-swell capabilities. The interlayer space occupied by the exchange cations can be increased from zero to several hundred Angstroms depending upon the variety of cations, the charge density on the silicate sheets, the variety of solvent and the partial pressure of solvent in equilibrium with the solid phase (Pinnavaia, 1976). There interlayer cations can be readily replaced via simple ion-exchange mechanisms with a wide variety of cations including transition metals, organometallic complexes, and carbonium ions.

My interest, and that of many recent researchers, has centered upon the use of these naturally occurring minerals as possible supports for heterogeneous catalysis and as molecular sieves. Their high surface areas (800 m^2/g) and cation exchange capacities (0.70 - 1.50 milliequivalents/g) compare favorably with synthetically manufactured zeolites.

The idea of using altered smectites as commercial catalysts is not new. In the processing of petroleum for fuels, the first commercial catalytic process, catalytic cracking, employed an acid treated clay. It remained for Eugene Houdry to recognize the improved gasoline quality obtainable from decomposition reactions utilizing clay catalysts and to develop a commercial process, first put into operation in 1936. This utilized an acid treated smectite in a fixed-bed reactor operated cyclically (Satterfield, 1980).

Some polymerization reactions are presently catalyzed by H_3PO_4 on clays in fixed-bed reactors (Satterfield, 1980).

Possibilities exist for treated clays in the inexpensive replacement of nickel (Ni) and palladium (Pd) Raney catalysts for hydrogenation and methanation reactions, and supported silver (Ag) in oxidation reactions of ethene to ethylene oxide. Properly prepared smectites might also be economical alternatives to acid-catalyzed reactions such as catalytic cracking, hydrocracking, and isomerization reactions that presently employ zeolites.

Synthetic pillared clays also show potential for use when high selectivity is desirable in a catalyst. It has already been shown that Wilkinson cationic analog intercalates can yield less than one percent isomerization in the hydrogenation reactions of 1-hexene as opposed to 58 percent isomerization with conventional homogeneous reactions (Pinnavaia, 1979).

For smectites to be feasible as catalyst supports, their interlayer volumes must be preserved. High temperatures or the presence of chemical species which strip the exchange ions of their solvation sheaths may result in the irreversible collapse of the silicate sheets upon one another, rendering their internal surfaces inaccessible to adsorption and possible catalysis. These constraints can be overcome by the use of props that, upon removal of the solvent, prevent collapse of the clay layers, and hold their interlayer volume to a specific value. The numerical value of this constant volume and the temperature range over which it is preserved, depend upon the size and orientation of the prop, as well as the reactivity associated with its chemical constituents.

A number of organic materials introduced into the interlamellar regions of swelling clays have been quite successful in keeping the layers apart when the solvent is removed. (Barrer and Macleod, 1951; Knudson and McAtee, 1973; Mortland and Berkheiser, 1976; Traynor et al., 1978). While these synthetic pillared clays remain stable at low to moderate temperatures, within a temperature range of 250 - 500C, the previously cited organic materials decompose and fail to keep the silicate sheets from collapsing.

Most commercially significant catalytic processes, however, occur in the moderate to high temperature range of 250 - 550C. Props that are thermally stable throughout this extended range have been sought, and some degree of success has been achieved. Aluminum hydroxides (Lahav et al., 1978), zirconyl chloride (Yamanaka and Brindley, 1979), and complex salts of 1, 10 - phenanthroline or bypyridyl (Loeppert et al., 1979) intercalates fired to high temperatures (550C) have been reported to be thermally stable.

Another promising attempt to develop a thermally stable pillared clay has involved the intercalation of silica in smectites (Endo et al., 1980). The elucidation of this particular mechanism for the intercalation of Si compounds in smectites, is the scope of the research reported here.

PART I

Mechanisms of Interaction for Smectites and the Tris(acetylacetonato)silicon(IV) Cation

Introduction

The successful preparation of thermally stable pillared clays from the intercalation of silica in smectites has been reported (Endo et al., 1980). This involved several chemical treatments and many firings at different temperatures. Actual preparation proceeds through the intercalation of tris(acetylacetonato)silicon(IV) cations into the interlamellar regions of smectites. The mechanism forming this precursor, however, has not previously been fully explained. The objective of this study was to provide more information about the mechanism of formation.

The hydrolysis product, $Si(OH)_4$, is thought to be an interlamellar intermediate in the successful preparation of the silica props that give the pillared smectite its thermal stability. For this reason, a study of the intercalation process included characterization of the hydrolysis reaction, both in solution and at the clay surface. Ultra-violet and infra-red spectrophotometry provide convenient quantitative techniques for the two different hydrolysis environments, respectively. To ascertain whether intercalation of the tris(acetylacetonato)silicon(IV) cation proceeds via a cation exchange process, counterion desorption was quantitatively monitored by flame emission and atomic absorption spectrophotometry. Three homoionic montmorillonites were prepared to contrast the effects of exchange ion upon the adsorption process as well as allowing definitive proof for the suspected role of ion exchange.

The delineation of solvent and counterion effects upon clay interlayer volume were aided by x-ray diffraction information, which also allows a means of assessing the relative extent of interlayer adsorption. The resulting information, taken in concert, was then used to develop an adsorption model from which a mechanistic interpretation was derived.

Experimental Methods

The smectites studied were montmorillonites of two types: hectorite, obtained from the Baroid Division of National Lead Industries, and bentonite, obtained from the American Colloid Company. Homoionic smectites were prepared from the less than two micron fraction of these naturally occurring forms (in 1% weight to volume suspensions) by equilibration with saturated aqueous solutions of the appropriate metal chloride salts. Dialysis of the resulting sols continued until they were free of excess salts as evidenced by the negative chloride ion test with $AgNO_3$. Lyophilizing, then rendered the clays free of excess water (H. van Olphen, 1977). Sodium, Mg, and Co homoionic smectites were each prepared in this manner.

One hundred mg of each prepared smectite was then washed repeatedly with saturated ammonium acetate solution until 100 ml were collected for each. The extracts were then analysed via flame emission spectrophotometry (for the Na clay) and atomic absorption spectrophotometry (for the Mg and Co clays). Cation specific exchange capacities for each were calculated, and found to be 0.84, 0.85, and 0.75 milliequivalents per gram of air dried clay for the Na, Mg, and Co-montmorillonites, respectively.

Oriented clay films, suitable for x-ray diffraction and infra-red absorption studies, were prepared by evaporation of aqueous suspensions (70 mg clay/30 ml water) under ambient conditions onto an area of 22.9 square centimeters per film.

The tris(acetylacetonato)silicon(IV) cation had already been prepared as the hydrogen dichloride anion salt by reaction of silicon tetrachloride with 2, 4 pentanedione (acetylacetone) using benzene as the solvent, according to the method of Riley et al., (1963). The prepared salt was stored under vacuum.

Solvolysis and adsorption information regarding the Si complex cation were determined using a Beckman DK-2A scanning double beam ratio recording UV-visible spectrophotometer. Solvolysis information regarding the Si complex cation was obtained in both water and acetone. Hydrolysis rates for the Si complex cation at the clay surface were obtained via a Beckman IR7 scanning double beam infra-red spectrophotometer. A Philips x-ray diffractometer employing Cu K-alpha radiation was used to determine the d(001) repeat spacings of the various smectites under investigation. Counterion desorption values, both in water and acetone, were determined for sample solutions containing Na, Mg, or Co. All metal concentrations were determined using a Perkin-Elmer 503 double beam atomic absorption spectrophotometer with a deuterium arc background corrector.

For adsorption and cation exchange experiments, approximately 250 mg of each variety of homoionic smectite was allowed to solvate in 500 ml of water or acetone for at least 24 hours prior to addition of the Si complex cation. Fifty ml of supernatant was then removed to beused as a blank. The Si complex cation was added to the clay-solvent system by first dissolving in 500 ml of solvent (water or acetone) a weighed quantity of the Si complex salt corresponding to fractions or multiples of the CEC equivalent of the particular clay being investigated. Fifty ml of Si complex cation solution was then removed to be used as a reference standard that was compared (when diluted 1:2) with the sample solutions over time. The remaining 450 ml of Si complex cation solution was immediately added to the 450 ml of clay - solvent suspension remaining. Small aliquots (20ml or less) were removed from the sample vessel periodically and immediately analyzed for the concentration of Si complex cation remaining in solution. These values were compared to similar values obtained for the reference standard solution. Temperature was kept at 4C for the water system and 25C for the acetone system. Counterion desorption concentrations were later determined for each aliquot removed.

Hydrolysis data for Si complex cations residing at the clay surface were obtained from clay films immersed in water, or exposed to water vapor at a partial pressure equal to one. In both cases these studies were carried out at 25C and from clay films treated with 10 CEC equivalents of the Si complex cation in an acetone solution.

Results and Discussion

The tris(acetylacetonato)silicon(IV) cation, henceforth designated as $Si(acac)_3^+$, is an immediate dissociation product when its hydrogen dichloride salt is placed in a polar solvent such as water or acetone. The solid salt melts with decomposition in the 170C to 174C temperature range, as reported by Riley et al. (1963). The cation, shown in Figure 1, is an octahedral univalent complex. Acetylacetonate ligands form planar bidentate, univalent anionic chelates with Si. While Kekule structures may be successfully drawn for the chelate ring, physical evidence for aromaticity has not been forthcoming and is, therefore, not shown in the figure. Fay and Serpone (1968) concluded that if benzenoid ring auppents exist at all in charged metal Beta-diketonate complexes, they must be quite small.

The complex cation is known to undergo hydrolysis by the equation shown in Table 1. In water, the complex cation shows maximum absorption at 290 nanometers, while free acetylacetone shows its maximum at 273 nanometers. By monitoring the solution peak shift, via UV spectroscopy, from 290 to 273 nanometers, the ratios of the concentrations of complex present at given times to the original concentration of complex present at time zero were determined. Successive iterations at constant temperatures provided the data required to characterize the hydrolysis of the complex cation in solution. The time intervals required for the aforementioned ratios to be equal to 0.5 (the half-life of the hydrolysis reaction, i.e. $t_{1/2}$) were found to be highly temperature dependent. Many kinetic models were applied to this system with the result that first order kinetics best predicted the data. The

Figure 1. The tris(acetylacetonato)silicon(IV) complex cation showing the positions of the Beta-diketonate ligands. Bond lengths and angles are not drawn to scale. Hydrogen atoms are omitted for clarity.

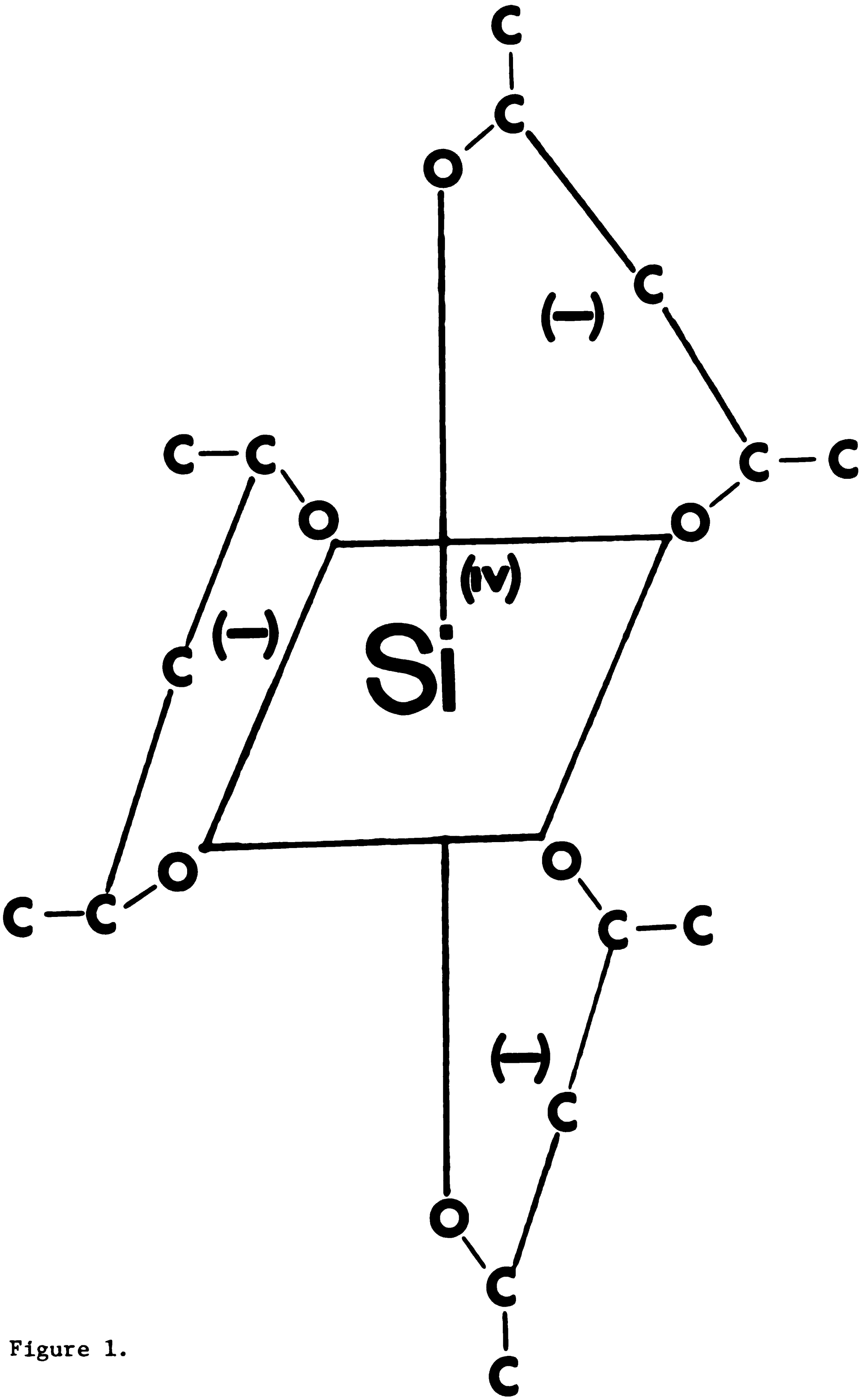

Figure 1.

Table 1. Solution Hydrolysis Reaction for $Si(acac)_3^+$:
$Si(acac)_3^+ + 5\ H_2O \longrightarrow Si(OH)_4 + 3Hacac + H_3O^+$

Reaction Temperature °C	Half-life of Reaction ($t_{1/2}$) min	r*
37	43	-0.998
35	52	-0.969
4	1560	-0.998

E_a = 20 Kcal/mole**

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*Linear regression first order correlation coefficients.

**The arrhenius activation energy for the reaction.

hydrolysis reaction is most likely a pseudo-first order process which are in agreement with the aquation kinetics of other octahedral complexes (Basolo and Pearson, 1958). Unlike the findings reported by Dhar et al., (1959), this reaction was found to be much more temperature dependent than pH dependent. While the pH data obtained in this study is in good agreement with the findings of Dhar et al., (1959), the earlier work was carried out between temperature extremes of 19.70C and 24.65C. Table 1 summarizes the effect of a wider temperature range on reaction half-life with corresponding linear regression correlation coefficients appropriate to first order kinetics. The calculated Arrhenius activation energy for this reaction is also reported.

Since the complex hydrolyzes in water, it is reasonable to suspect that it may hydrolyze in the presence of water at the clay surface. Homoionic montmorillonite films with Na, Mg, or Co occupying the cation exchange sites were treated with $Si(acac)_3ClHCl$ dissolved in acetone to retard hydrolysis. Basal spacings, d(001), of these films are reported in the "before hydrolysis" column of Table 2. Transmission infra-red spectra were run on the intercalate films between 1100 and 1800 wavenumbers. The resulting spectra coincide with the spectra reported by Thompson (1969) attributed to $Si(acac)_3^+$. Specifically, well defined bands at 1320, 1350, 1390, 1540, and 1555 wave numbers were observed and attributed to the complex cation residing at the clay surface. The 1390 cm^{-1} band was chosen to monitor hydrolysis rates at the clay surfaces, as this was the most prominent band attributed to the complex having per cent transmission greater than zero.

Table 2. Interlayer hydrolysis for the Following Reaction:

$$\frac{\text{Clay}}{\text{Si(acac)}_3^+} \xrightarrow{25^{\circ}\text{C}} \frac{\text{Clay}}{\text{Si(OH)}_4\ \ \text{H}^+} + 3\text{Hacac}$$

Original Counterion	Half-life of Reaction ($t_{1/2}$)	-r diffusion A/A_0	d(001)before hydrolysis	d(001)after hydrolysis
	hours		Å	Å
Na $P/P^o=1$	173	0.949	16.98	----
Na	163	0.943	16.98	15.77
Mg	474	0.909	16.98	15.49
Co	462	0.994	16.35	15.49

Data indicates reaction half-life ($t_{1/2}$) dependence on original counterion. Hyperbolic diffusion equation correlation coefficients (-r), and X-ray data taken before and after two weeks of hydrolysis are shown.

Two different hydrolysis environments were studied. The $Si(acac)_3^+$ intercalate films, prepared from homoionic Na-montmorillonite films were, exposed to water vapor at 100% relative humidity for a period of two weeks. $Si(acac)_3^+$ intercalated films prepared from homoionic Na, Mg, or Co-montmorillonite films were each immersed in liquid water for a period of two weeks. Both environments were kept at 25C. Spectra were obtained for each film, at hourly intervals early in the study, and less frequently thereafter, as changes proceeded less rapidly. Liquid water was allowed to evaporate from each film studied by placing the film in the IR beam prior to obtaining the spectrum. The 1390 cm^{-1} band, attributed to the complex at the clay surface, and the broad 1630 cm^{-1} band, attributed to water at the clay surface, were each monitored in transmittance mode and the data converted to absorbance values. Again, many kinetic models were tested for the two sets of absorbance values collected. The model that best fits the increasing appearance of water and decreasing surface concentration of complex cation is given by the hyperbolic diffusion equation. In its simplest form, this equation may be represented as: $A = mt^{1/2} + A_0$. The concentration of a given species, A, at some time, t, is related to its initial concentration, A_0, by the slope of a line, m, that is generated as a function of the square root of time. Linear regression correlation coefficients obtained by application of the hyperbolic diffusion model to the data are reported as the third column of Table 2. These relate unhydrolyzed complex remaining at the surface to the square root of elapsed time. The d(001) spacings obtained for the intercalated films at the conclusion of the two week period of hydrolysis are shown in the last column of Table 2. The interlayer hydrolysis equation given in the table shows free acetylacetone as a decomposition product that does not occupy the interlayer volume. This is supported by the absence of both the keto and enol bands associated with acetylacetone in all IR spectra collected. This may be an artifact of the drying process, however, as acetylacetone desorbs rapidly from the clay surface when exposed to the atmosphere (Parfitt and Mortland, 1968).

It is interesting to note that the half-life of the surface hydrolysis reaction at 25C (reported as column 2 of Table 2) is an order of magnitude greater than the corresponding half life in water solution even at 4C. The tabulated information also adds support to the importance of the original counterion occupying the cation exchange sites of the clay (shown as column 1 of Table 2). Apparently, the hydrolysis reaction, which in solution is a first order process, becomes diffusion controlled when the complex cation resides in the interlayer. Larger hydration sheaths associated with the Na cation and the attendant greater hydrated basal spacings of the Na-clay result in less constrained and more "water rich" environments than in the Mg or Co clays. The hydrolysis half-life of the complex on the Na clay is then, predictably shorter than those measured for the Mg or Co clays. Hydrated Mg or Co-montmorillonites, whose basal spacings are both about 20 Angstroms, show similar half-lives, as expected.

Constrained volume and fewer water molecules must surely be responsible for the diffusion controlled character of the hydrolysis reaction in the clay interlayer. The much greater stability of the complex at the clay surface, however, may not be entirely due to these factors. One feature of the Si-ligand bond, in the complex cation, is the transfer of positive charge. The ligand field effect manifests itself as delocalization of the acetylacetonate pi electrons onto the central Si ion, accompanied by delocalization of the positive charge, associated with Si, onto the ligand. This feature imparts stability to the complex, whether it exists free in solution or resides in the clay interlayer. The added field effect of the anionic clay surface upon the complex cation may provide additional motivation for electrons and positive holes to further change places, resulting in more pi character for the Si-O bond, and even greater stability for the complex at the clay surface.

The original intent of this research project was to obtain adsorption isotherms for $Si(acac)_3^+$ on various homoionic smectites and to determine whether or not this process could be viewed as a cation exchange reaction. Typically, adsorption phenomena are reported as amount of adsorbate adsorbed per weight of adsorbent versus various equilibrium solution concentrations of adsorbate. Two facts complicate reporting the results of this research in typical fashion. First, solution hydrolysis in water proceeds ultimately to an "equilibrium" state where zero concentration of complex is present irrespective of initial concentration. Second, hydrolysis continues at the clay surface, so that the amount of adsorbate present per weight of clay is demonstrably time dependent.

For these reasons, a predictive description that incorporated the suite of dynamic processes involved in the clay-solvent-$Si(acac)_3^+$ system was sought.

Early attempts involved acetone as the solvent, to retard hydrolysis of the complex cation. The success of the acetone system was limited, however, by difficulties associated with the reliable quantitative determination of $Si(acac)_3^+$ in the presence of acetone and acetylacetone. Counterion desorption data were obtained by atomic emission or absorption spectrophotometry depending upon the metal cation studied.

Sodium, Mg, and Co homoionic montmorillonite were each treated with two times their equivalent cation exchange capacities with $Si(acac)_3^+$. The d(001) spacings of 17 Angstroms indicated successful intercalation. For the Na and Mg-smectites,the intercalation process carried out in acetone, apparently does not proceed primarily as a cation exchange process. Fractional CEC equivalents of Na and Mg were desorbed from their respective homoionic clay surfaces (0.04 and 0.06 CEC, respectively) after 48 hours of exposure to the complex in acetone solution. Under similar conditions, however, the Co-smectite underwent complete ion exchange, desorbing 1.00 CEC equivalents of Co to the acetone solution, in the same time period. Before addition of the complex, the Co-clay was pale pink in color. Upon addition of the complex, the clay turned progressively bluer and in time, the blue color had spread to the acetone solution. Both the color change and the ion exchange properties of the Co system may be explained from the electronic configuration of the divalent Co cation.

All hydrated Co(II) salts are red or pink and contain octahedrally coordinated $Co(H_2O)_6^{+2}$ ions. These are probably responsible for the untreated Co-montmorillonite's color. Many permutations of the species involved were assembled in an attempt to mimic the pink to blue color change. The simplest combination which produced the blue color occurred when acetone and HCl were added to an aqueous $CoCl_2$ solution. The tetrahedral anion $CoCl_4^{-2}$appears green, blue, or purple in solution (Cotton and Wilkinson, 1972), but seems a less likely candidate in view of the preference of d^7 systems for ketones. Also, one would expect formation of an anion at the clay surface to be disfavored. Even if successful, electrostatic repulsion should rapidly drive the anion from the field of the clay surface rather than exhibit the gradual color migration observed in this clay system. Instead, Co(II) may be successfully solvated by acetone, displacing water, and then proceed to a neutral complex of the form CoL_2X_2 where L are acetone ligands and X are chloride anions (Cl^-). This neutral species, ostensibly at or near a cation exchange site, could then be easily replaced by the Si complex cation.

The successful solvation of Co(II) by acetone is made possible by the electronic configuration of the metal ion. The filled shell inert gas electronic configurations of the hydrated Na and Mg cations are much less amenable to complex formation, and acetone may merely dehydrate these. Stripped of their hydration sheaths, these ions move closer to the clay surface, are held more rigidly, and are less apt to exchange with the Si complex cation. Complex adsorption exceeds counterion desorption. This is similar to the results of adsorption studies performed on smectites with orthophenanthroline or bipyridyl complexes (Loeppert et al., 1979).

If intercalation is carried out in water, rather than acetone, a very different and more complicated picture emerges that reinforces the need for a predictive model. Sodium, Mg, and Co-montmorillonite films were each treated with $Si(acac)_3ClHCl$ in concentrations equivalent to 0.5, 1, and 2 times the homoionic clays' respective cation exchange capacities. All sets were studied at 4C to slow solution hydrolysis of

Table 3. Si(acac)$_3^+$ Adsorption on Mg-Montmorillonite in Water

Average Elapsed Time in hours	R Si(acac)$_3^+$ Standard in CEC equivalents	H Si(acac)$_3^+$ Sample in CEC equivalents	S Si(acac)$_3^+$ Surface in CEC equivalents	Mg Sample in CEC equivalents
0.11 t_0	2.02	1.96	0.060	0.09
0.81 t_1	1.88	1.81	0.074	0.12
4.00 t_2	1.55	1.51	0.056	0.15
20.74 t_3	1.22	1.00	0.239	0.23
23.87 t_4	1.00	0.93	0.122	0.24
44.82 t_5	0.65	0.60	0.114	0.30
115.17 t_6	0.13	0.15	0.062	0.33

Surface $t_{1/2} = 474$ hours

$S_{t_0} = (R_{t_0} - H_{t_0})$

$S_{t_i} = (D_{t_i - t_{i-1}} * S_{t_{i-1}}) + ((H_{t_{i-1}} * [R_{t_i}/R_{t_{i-1}}]) - H_{t_i})$

for all $i > 0$.

the complex. Concentrations of complex cation were obtained for samples (solutions exposed to the clay) and standards by UV spectroscopy. Counterion desorption was ascertained by atomic emission or absorption spectrophotometry. Table 3 is offered as an example of a data set. The information presented is for Mg-montmorillonite exposed to concentrations of $Si(acac)_3^+$ equivalent to twice the clay's cation exchange capacity. All columns, except the one headed "S", represent direct measurements made on the system. Entries in columns "R" and "H" represent the solution concentrations of the $Si(acac)_3^+$ cation in reference standards and sample solutions, respectively. Note the monotonic decrease in concentration with increase in elapsed time. The entries in the last column show the monotonic increase in Mg^{+2} desorbed to solution with time. The entries in the column headed "S" are each the surface concentration of $Si(acac)_3^+$ at a particular time, t_i. If this were a typical, well behaved system we could say $S_{t_i} = (R_{t_i} - H_{t_i})$. This equation assumes the complex hydrolyzes at the same rate whether it is free in solution or residing at the clay surface. Clearly, this equation is inadequate.

The equation shown at the bottom of Table 3 was therefore developed. The development of this equation evolved from an attempt to incorporate all the relevant information collected, into a single expression reflecting the dynamic simultaneous processes occurring in the system. The column headings of Table 3 correspond to variables in the equation shown.

S_{t_i} is the surface concentration of $Si(acac)_3^+$ in CEC equivalents calculated for time t_i.

R_{t_i} is the reference standard solution concentration of $Si(acac)_3^+$ in CEC equivalents measured at time t_i.

H_{t_i} is the sample solution concentration of $Si(acac)_3^+$ in CEC equivalents measured at time t_i.

D is a dimensionless fraction such that for all $t_i > 0$, $D < 1$, and for $t = 0$, $D = 1$. So, $D_{t_i - t_{i-1}}$ is the fraction of $Si(acac)_3^+$ remaining intact at the clay surface at the end of time interval $(t_i - t_{i-1})$.

It is calculated from the hyperbolic diffusion equation using the ordered pairs (0, 1) and ($t_{1/2}$, 0.5), where the first entry in the ordered pair is elapsed time, and the second entry in the ordered pair is the fraction of complex remaining at the surface given the initial surface concentration ratio is normalized to 1.

Having established the identity of these variables, their iterative manipulation according to the equation ultimately produces the entries in column "S" of Table 3.

The manipulations are examined:

$[R_{t_i}/R_{t_{i-1}}]$ yields the fraction of $Si(acac)_3^+$ remaining in the reference standard solution at the end of time interval $(t_i - t_{i-1})$, i.e. at time t_i. It is the reference standard solution analog of D.

The product $(D_{t_i - t_{i-1}} * S_{t_{i-1}})$ is that part of the surface concentration of $Si(acac)_3^+$ remaining at the end of time interval $(t_i - t_{i-1})$, given the surface concentration was $S_{t_{i-1}}$ at time t_{i-1}. This value, in CEC equivalents, is affected only by desorption or surface hydrolysis of $Si(acac)_3^+$ predicted by the counterion specific hyperbolic diffusion equation. By itself, it does not take into account additional

adsorption or desorption during this time interval; however, the remaining manipulations do:
$(H_{t_{i-1}} * [R_{t_i}/R_{t_{i-1}}])$ predicts a value for H_{t_i}, i.e., sample solution concentration of $Si(acac)_3^+$ if only solution hydrolysis affects the value of $H_{t_{i-1}}$ over the time interval (t_i-t_{i-1}).
But H_{t_i} is a measured concentration and is, therefore, compared to the predicted value by the expression:
$((H_{t_{i-1}} * [R_{t_i}/R_{t_{i-1}}])-H_{t_i})$.
Three possible cases result:

Case 1 is the trivial case, where the predicted and measured values are identical. The difference is zero, and S_{t_i} is equal to the first parenthetical expression in the equation of Table 3.

Case 2 occurs when the predicted value is greater than the measured value. A positive difference implies that the rate of adsorption of the complex is greater than the rate of desorption over the time interval (t_i-t_{i-1}). The sum of the first parenthetical expression in the equation and this difference is now the value of S_{t_i}.

Case 3 occurs when the predicted value is less than the measured value. A negative difference implies that the rate of adsorption of the complex is slower than the rate of desorption over the time interval (t_i-t_{i-1}). The first parenthetical expression in the equation is reduced by the absolute value of the difference and this now becomes the value for S_{t_i}.

This iterative feedback process is followed for all $i>0$ and generates the "S" column of Table 3. The process is initiated at t_0 so that $S_{t_0} = (R_{t_0}-H_{t_0})$ is the first and only entry of the "S" column that cannot rely upon the equation developed here.

Counterion desorption and $Si(acac)_3^+$ adsorbed as a function of time for the Na, Mg and Co-montmorillonites is shown in figures 2, 3, and 4, respectively. The solid lines indicate the counterion desorption over time and are marked 0.5, 1, and 2. So marked, they distinguish the three levels studied for each clay, i.e., initial solution concentrations of $Si(acac)_3^+$ corresponding to 0.5, 1, and 2 times the equivalent cation exchange capacities of the particular clay. These solid lines contain open circles indicating the measured counterion data points. Individual solid points indicate the amount of $Si(acac)_3^+$adsorbed to the clay surface at particular times. The initial solution concentration set to which each point belongs is distinguished by the shape of the point. Triangular points belong to the 0.5 CEC equivalent set. Square points are members of the 1 CEC equivalent set. Circular points indicate the two CEC equivalent set.

All individual points have been generated using the iterative equation described earlier.

For the Na-montmorillonite system (Figure 2), complex adsorption is maximized in the first few minutes. So initially, the system is primarily a cation exchange process. The large $Si(acac)_3^+$ complex covers the surface of the clay, displacing only that amount of Na necessary to achieve neutrality. Later, as solution hydrolysis outruns surface hydrolysis, mass action drives some $Si(acac)_3^+$ off the surface making room for readsorption of the counterions. This is exaggerated by lower initial solution concentrations of $Si(acac)_3^+$. If no cationic hydrolysis product were to occupy the interlayer, one would eventually expect that the counterion would be completely readsorbed. However, protons are produced by the hydrolysis reaction both in the interlayer

Figure 2. $Si(acac)_3^+$ adsorbed and Na released from Na-montmorillonite as a function of time. The solid lines show Na desorbed over time for initial solution concentrations of $Si(acac)_3^+$ of 0.5, 1, and 2 CEC equivalents, respectively. Open circles indicate measured data points. Calculated surface concentrations of the complex cation are shown as points: triangles, squares, and circles correspond to surface concentrations of complex cation calculated for data sets each having initial solution concentrations of 0.5, 1, and 2 CEC equivalents of $Si(acac)_3^+$, respectively.

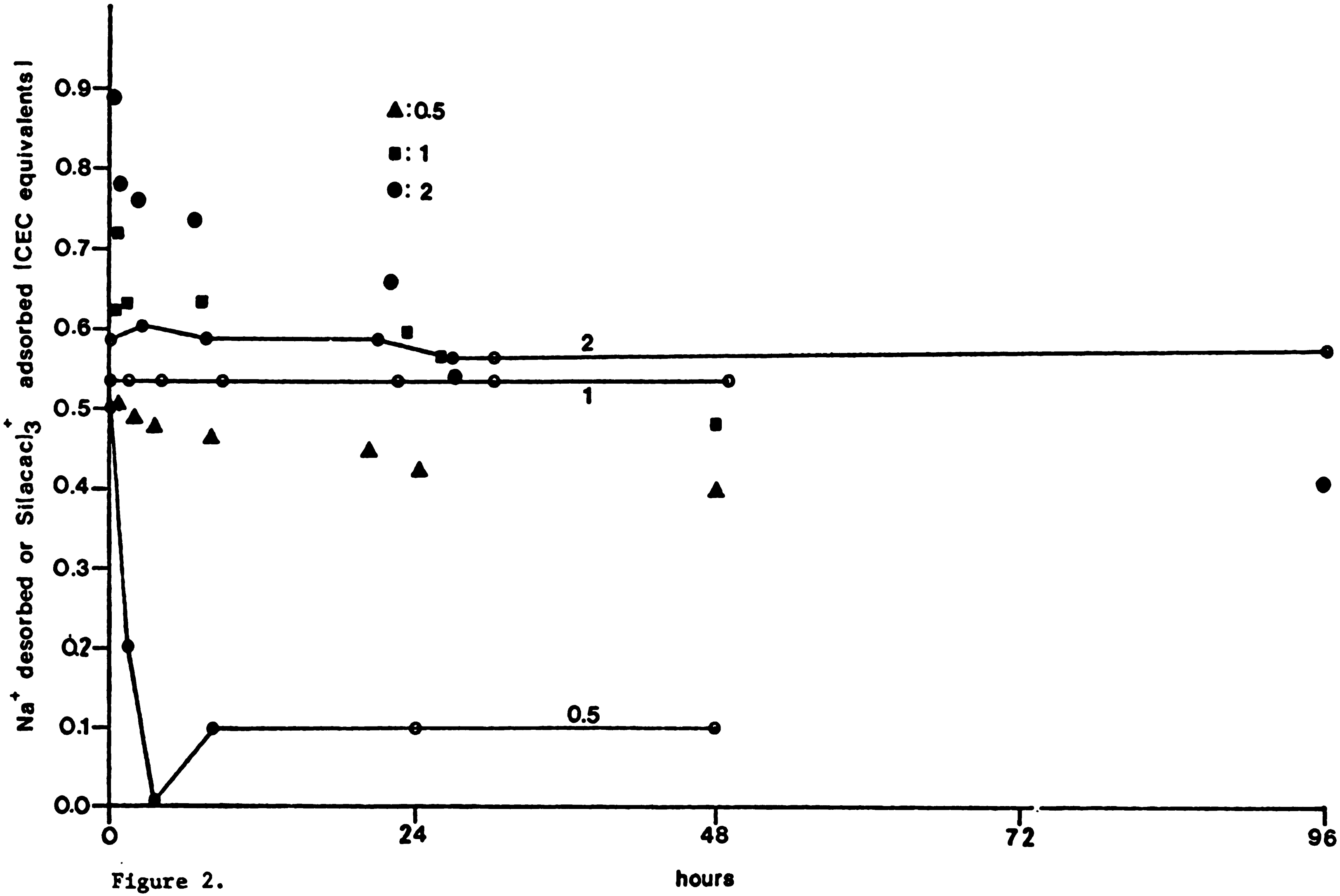
Na⁺ desorbed or Silacacl₃⁺ adsorbed (CEC equivalents)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
▲: 0.5
■: 1
●: 2
2
1
0.5
0
24
48
72
96
hours

Figure 2.

Figure 3. $Si(acac)_3^+$ adsorbed and Mg released from Mg-montmorillonite as a function of time. The solid lines show Mg desorbed over time for initial solution concentrations of $Si(acac)_3^+$ of 0.5, 1, and 2 CEC equivalents, respectively. Open circles indicate measured data points. Calculated surface concentrations of the complex cation are shown as points: triangles, squares, and circles correspond to surface concentrations of complex cation calculated for data sets each having initial solution concentrations of 0.5, 1, and 2 CEC equivalents of $Si(acac)_3^+$, respectively.

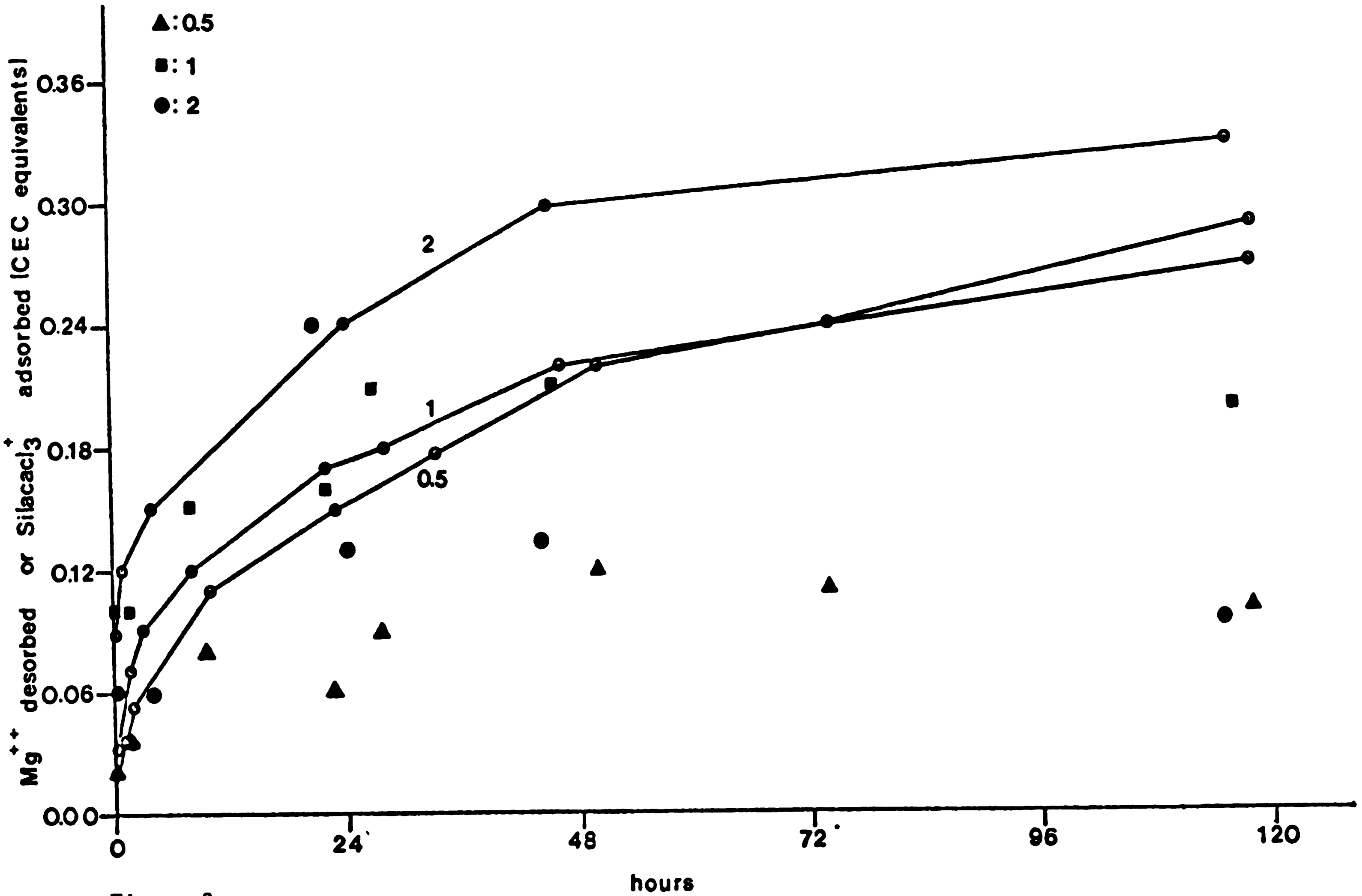
▲: 0.5
■: 1
●: 2
2
1
0.5
0.36
0.30
0.24
0.18
0.12
0.06
0.00
Mg^{++} desorbed or $Silacacl_3^+$ adsorbed (CEC equivalents)
0
24
48
72
96
120
hours

Figure 3.

Figure 4. $Si(acac)_3^+$ adsorbed and Co released from Co-montmorillonite as a function of time. The solid lines show Co desorbed over time for initial solution concentrations of $Si(acac)_3^+$ of 0.5, 1, and 2 CEC equivalents, respectively. Open circles indicate measured data points. Calculated surface concentrations of the complex cation are shown as points: triangles, squares, and circles correspond to surface concentrations of complex cation calculated for data sets each having initial solution concentrations of 0.5, 1, and 2 CEC equivalents of $Si(acac)_3^+$, respectively.

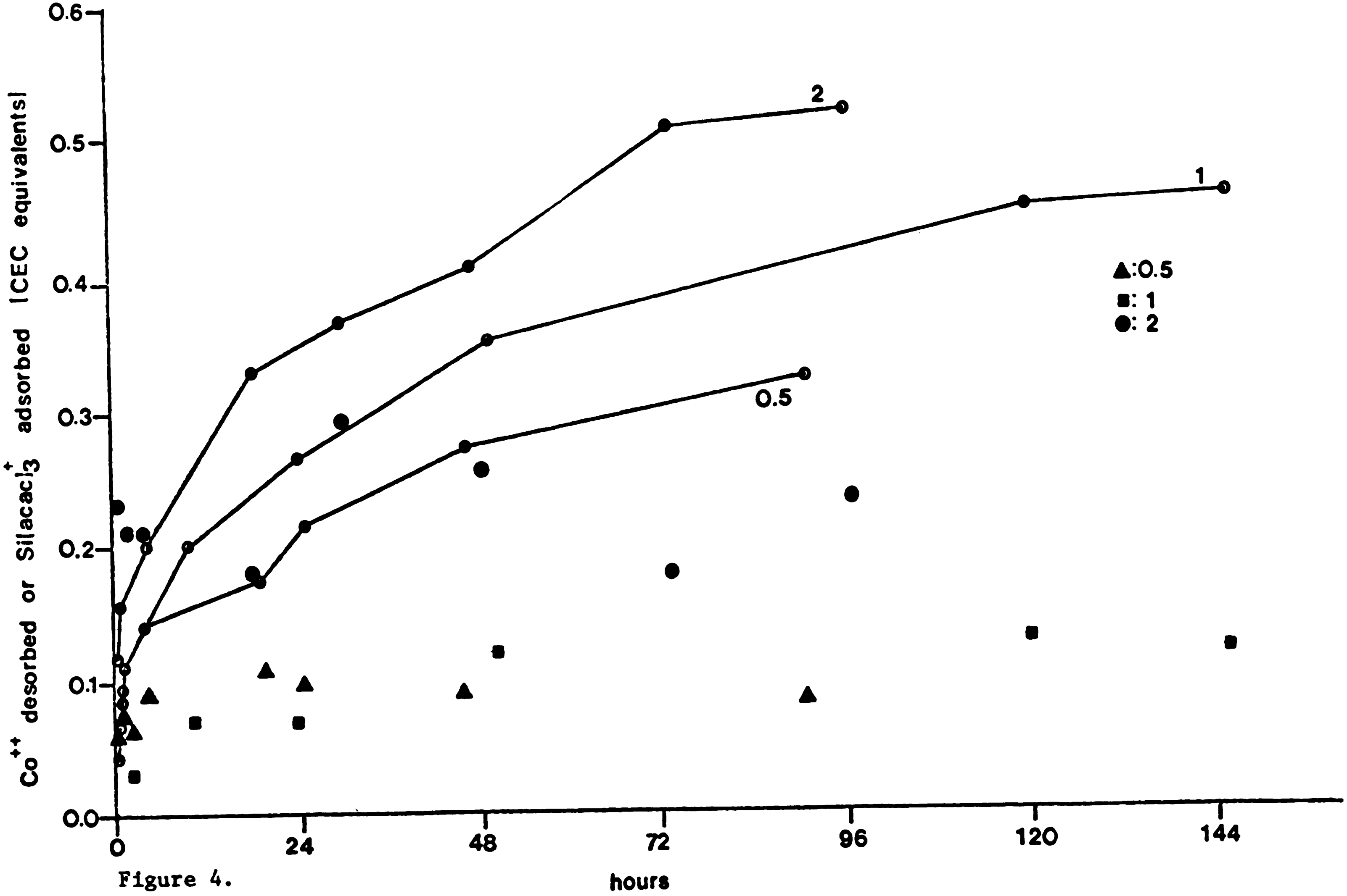
Co^{++} desorbed or Silacac$_3^+$ adsorbed (CEC equivalents)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
24
48
72
96
120
144
hours
2
1
0.5
▲: 0.5
■: 1
●: 2

Figure 4.

and in solution. The counterion must now compete, not only with the diminishing number of complex cations for exchange sites, but also with the increasing number of surface hydrolysis protons produced in the interlayer that need not diffuse into it. Solution counterion concentration then reaches a constant level in time. At higher initial solution concentrations of complex cation, initial exchange takes place followed by additional $Si(acac)_3^+$ physically adsorbing to the clay, probably with Cl^- accompanying it into the interlayer, to preserve neutrality. Some of the Na cations are sterically blocked by the additional $Si(acac)_3^+$ and remain unavailable for exchange. Counterion flux from surface to solution and vice versa are probably damped in this way.

The Mg and Co systems (Figures 3 and 4, respectively) show less affinity for the complex cation. This probably arises from the smaller hydration spacings associated with these clays and their more restricted interlayer volumes when compared to the Na-montmorillonite system. This idea is supported by the time position of maximum complex adsorption. The Mg and Co systems do not achieve maximum complex adsorption until many hours after initial addition of the complex solution, suggesting diffusion controlled adsorption. Also, unlike the Na system, counterion solution concentrations increased regularly with time, until reaching a plateau.

Subtle differences contrast the Mg and Co systems. Complex adsorption seems slightly favored by the Mg system when compared to Co. Cobalt, however, is desorbed in greater amounts than Mg. Interlayer volume differences are not great enough to explain these disparate phenomena. This apparently opposite behavior may be due to the different chemical properties of the two counterions themselves. The divalent Mg cation regards ketones with a nonchalance unshared by the electron-poor d orbitals of Co(II). Indeed, Co(II) is known to form tetramers of bis(acetylacetonato)cobalt(II) (Cotton and Wilkinson, 1972). Also, Co(acac)$_3$ is also known to be stable (Basolo and Johnson, 1964).

While no physical evidence can be offered to support the existence of these moieties in the Co-montmorillonite system, free acetylacetone is present in increasing abundance. And, if Co could successfully abstract the bulky acetylacetonate anion from tetravalent Si (whose electronic configuration is the same closed shell as Ne, Na$^+$, or Mg^{++}), then Co desorption would be favored when compared with the corresponding Mg system. Initially, Si(acac)$_3{}^+$ in the Co-montmorillonite interlayer could not long survive intact. Interlayer hydrolysis would be initially promoted resulting in protons capable of occupying the exchange sites formerly occupied by Co. This scenario may then prevent, or at least delay, appreciable adsorption by the remaining Si(acac)$_3{}^+$.

Figure 5 summarizes the major reactions known to take place in the systems studied.

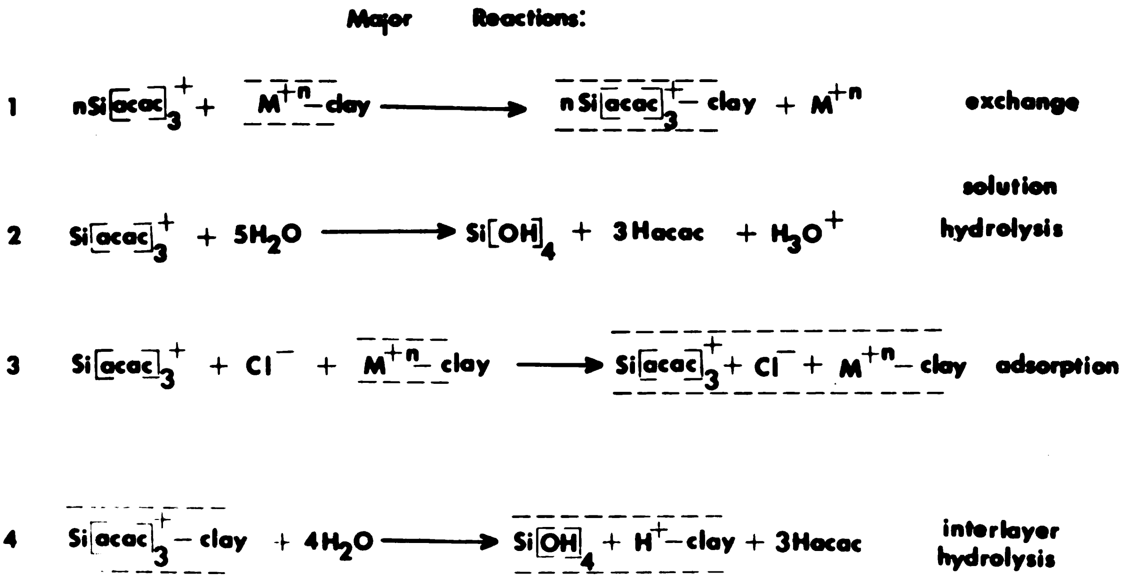

Figure 5. A pictorial summary of the major reactions that are known to occur during homoionic montmorillonite-$Si(acac)_3^+$ interaction.

PART II

Interaction of Smectites with Phenyltrichlorosilane

Introduction

The interaction of smectites with chlorosilanes has been studied before (Aragon De La Cruz et al., 1973). The previous study, however, was not an adsorption study, nor was it carried out in the presence of a solvent.

The motivation for the research reported here, was in the possible use of silane intercalates for the production of thermally stable pillared clays, as an alternative to the $Si(acac)_3^+$ pathway. The problem was to determine if appreciable adsorption of silanes by smectites occurred and, if so, to quantitate it and elucidate the mechanism of interaction.

Four homoionic montmorillonites were chosen to determine the extent of counterion interaction upon adsorption and intercalation. Counterion specific adsorption isotherms contrast the differing effects of valence, electron orbital chemistry, and d(001) basal spacings upon the adsorption of the silane, as well as provide a quantitative description of the completeness of the process.

Additionally, x-ray diffraction provides the tool for determining the extent of solvation, the presence of a successful intercalate, and (combined with different heat treatments) the degree of thermal stability. Infra-red spectrophotometry was used to measure quantitatively the degree of adsorption by monitoring solution depletion of the silane. The use of bentonite films (rather than lyophilized powders) along with IR spectrophotometry provides a means of corroborating x-ray data that suggest the presence of silanes in the clay interlayer.

The compilation of this information was then utilized for the understanding of how phenyltrichlorosilane forms intercalates with smectites.

Experimental Methods

The smectites studies, Na, Mg, Co(II), and Cu(II) homoionic montmorillonites, were each prepared from naturally occurring Wyoming bentonite (obtained from the American Colloid Company). The method of preparation was analogous to that reported in the Experimental Methods section of Part I.

Phenyltrichlorosilane and methyltrichlorosilane were both obtained from the Alfa Division of the Ventron Corporation (lot numbers 011078 and 113077, respectively). Density data, from which molar concentrations could be calculated, were taken from the Handbook of Organometallic Compounds.[1]

All adsorption isotherm data were collected using benzene as the solvent. Homoionic clay films were prepared in the manner described in the Experimental Methods section of Part I and used throughout this unit

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[1] (1968), translated from the Japanese, W. A. Benjamin, Inc.

of research (rather than the lyophilized powdered clays employed in some of the adsorption studies reported in Part I). The weights of the clay films prepared were between approximately 60 and 70 milligrams each. All films were allowed to solvate in either 15 or 20 ml of benzene for 24 hours prior to the addition of the silane. Quantitation standards were prepared by adding the same volume of silane to varying volumes of benzene. Quantitative measurements of the phenyltrichlorosilane in standard and sample solutions, and qualitative identification of the silane at the clay surface, were both monitored at the 1426 cm^{-1} infra-red band after 24 hours of exposure to the silane. Sample sets consisted of 10, 20, 50 or 100 microliters of silane added added to the solvated clay films in benzene.

An infra-red liquid cell with KBr windows was constructed to allow a solution path length of 1.8 millimeters. This was necessary due to the relatively small molar absorptivity of phenyltrichlorosilane at 1426 cm^{-1}.

Basal spacings, d(001), of untreated, solvated, and silane treated smectite films were each obtained by x-ray diffraction.

Color changes that occurred in the Co and Cu-clay films were verified and contrasted by UV-visible spectrophotometry.

All analytical methods mentioned in this section, employed the corresponding instrumentation specified in the Experimental Methods section of Part I.

Additionally, esr spectra at 25C, were obtained for Cu and Co montmorillonite films. Both untreated, and phenyltrichlorosilane treated films were studied. A Varian E-4 esr spectrometer was used for this comparison.

Results and Discussion

Benzene is miscible with phenyltrichlorosilane, yet does not react with it. The presence of phenyltrichlorosilane in benzene may be measured quantitatively by infra-red spectrophotometry. For these reasons, benzene was employed as the solvent in this study.

Sodium, Mg, Co(II), and Cu(II) homoionic montmorillonite films were each allowed to solvate in benzene prior to the addition of phenyltrichlorosilane. Infra-red spectra were obtained for each clay film, and each sample solution containing it. The 1426 cm^{-1} band allowed quantitative determination of the silane in solution, as well as qualitative identification of the compound adsorbed to the clay film. This band corresponds to the asymmetric ring stretch of the phenyl group attached to Si in the silane studied.

The adsorption isotherms obtained for each system are depicted in Figure 1. Of the homoionic montmorillonites investigated, their affinity for phenyltrichlorosilane ranks, in increasing order; Na < Mg < Co < Cu. Corresponding chemical symbols indicate the homoionic montmorillonite to which each adsorption isotherm belongs (Figure 1).

The d(001) basal spacings for each clay film are reported at various stages of the experiment, as well as their color (Table 1).

Note that all films, except Cu-montmorillinite, have been swollen by benzene. And, after one hour at 100C, all have collapsed to smaller spacings than their ambient "air-dry" hydrated values. Benzene solvation does not alter the color of any of the clay films. The Cu(II)-montmorillonite, does however, change gradually from green to yellow upon addition of phenyltrichlorosilane. The yellow color is

Figure 1. Adsorption isotherms obtained for phenyltrichlorosilane on Na, Mg, Co(II), and Cu(II) homoionic montmorillonites in benzene.

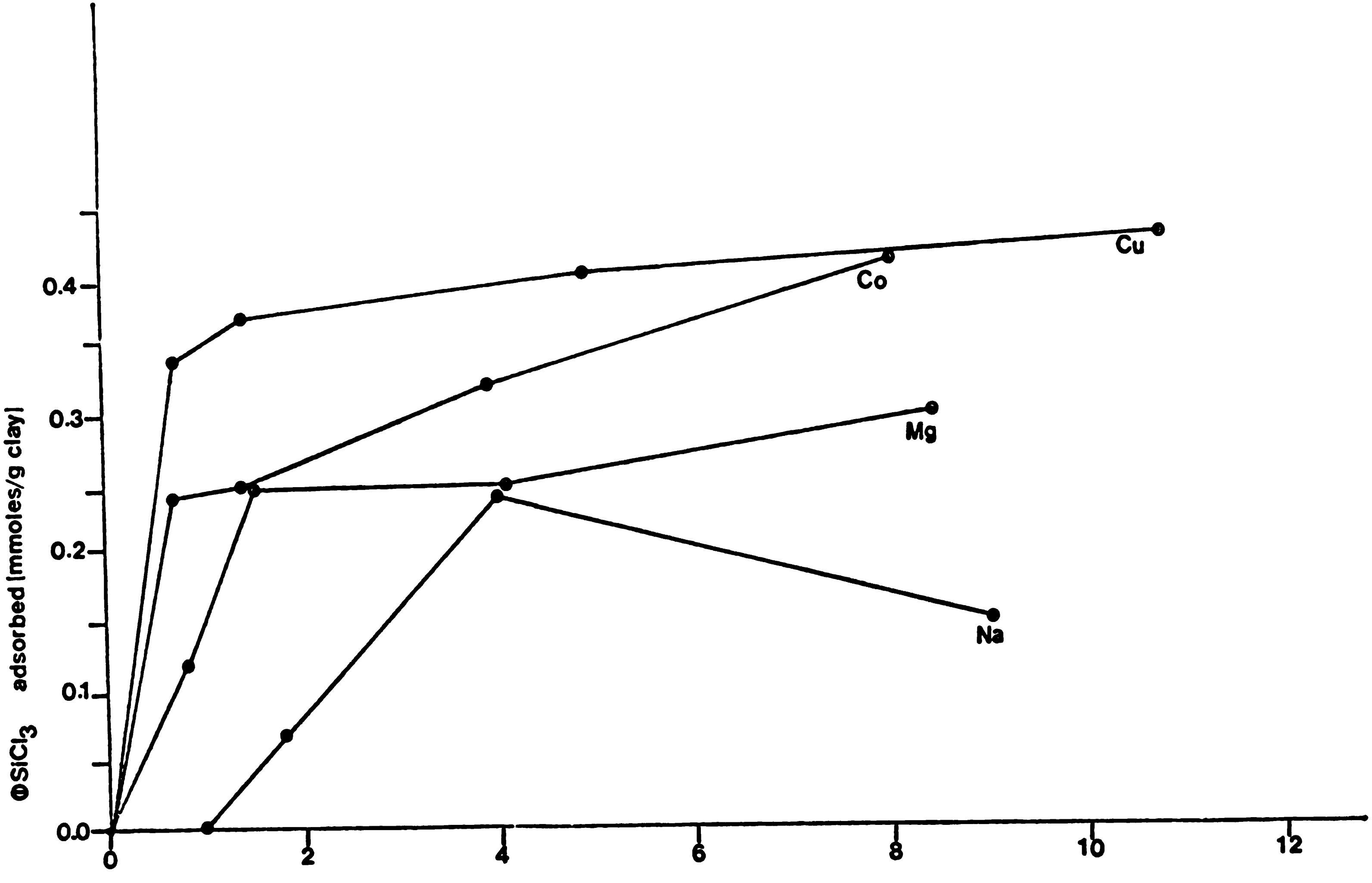
ΦSiCl3 adsorbed (mmoles/g clay)
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
12
Cu
Co
Mg
Na
equilibrium solution concentration of ΦSiCl3 (mmoles/g clay)

Figure 1.

Table 1. Basal Spacings, and Colors of Homoionic Montmorillonite Films*.

Bentonite Film	"Air Dry" d(001) Angstroms	Benzene Solvated d(001) Angstroms	(Solvated) 100 C d(001) Angstroms	Benzene Solvated, Silane Treated d(001) Angstroms	(Treated) 100 C d(001) Angstroms
Na	10.3 W	10.5 W	9.5 W	10.3 W	9.8 W
Mg	13.7 W	14.2 W	13.6 W	14.2 W	14.2 W
Co	12.6 P	14.2 P	12.3 P	14.2 P	13.2 B
Cu	12.2 G	12.1 G	11.9 G	14.2 Y	12.2 YY

*W=White, P=Pink, G=Green, B=Blue, Y=Yellow, and YY=Intense Yellow.

intensified by removing the clay from solution and heating it to 100C. The yellow color associated with the Cu-clay does not migrate to the benzene solution. It is interesting to note that when benzene is allowed to evaporate from the clay films prior to heating, the colors of Table 1 result. However, if the Cu-clays are heated immediately after removal from the benzene solution, the Cu-clays left untreated with phenyltrichlorosilane become red indicating presence of the Cu-benzene charge transfer complex (Doner and Mortland, 1969). The silane treated Cu-clay behaves as before, turning yellow.

The Co(II)-montmorillonite, treated with the silane, experiences a less drastic pink to blue color change only upon heating. Further heating to 300C fully collapses all clays investigated. The clays appear charred and black; all color is lost.

It was felt that the yellow color of the treated Cu-clay might indicate the presence of another charge transfer complex. Esr data, however, indicated insignificant changes in the g value when Cu(II)-montmorillonite is exposed to phenyltrichlorosilane.

To help understand the different affinities the four homoionic montmorillonites exhibit for phenyltrichlorosilane, and to more specifically examine the color changes that take place, Cu(II) and Co(II)-montmorillonite films were prepared on quartz discs.

All were benzene solvated and half were exposed to 100 microliters of phenythrichlorosilane for twenty-four hours. Transmittance spectra were obtained for the clay coated discs throughout the visible light region. Raw transmittance data are reported in the first two rows of Tables 2 and 3. The spectrophotometer's transmittance baseline was adjusted to allow both phenyltrichlorosilane treated, and corresponding untreated clay spectra to be recorded on the same chart without overlap.

To establish differences between spectra, the spectra were assumed to be identical, and a linear transformation sought that could superimpose one upon the other. The spectra would be symmetric and their difference, a constant, attributed to baseline adjustment. The third row of Tables 2 and 3 report the differences between the transmittance of the untreated reference clay film (% TR, row 1) and the silane treated sample clay film (% TS, row 2) at roughly 50 nanometer increments. The mean value of row 3 and its associated standard deviation are determined statistically. Row 4, then, is the interval by interval tabulation of the sum of each entry in row 2 with the mean of row 3. If the reference and sample spectra are identical, the entries of row 4 should each equal their corresponding entries in row 1. If, however, they differ by more than one standard deviation, there is said to be a significant difference between the spectra. The statistical manipulation of the spectra confirm the eye's contradiction of identity. Row 5 reports whether the treated sample or the untreated reference clay is more transparent at each interval of wavelengths. Entries in row 6 (the absolute values of the differences between entries in row 1 and entries in row 4) indicate how much more transparent (in % T) is the sample or reference, in that particular interval. Row 7 indicates where the difference exceeds one standard deviation and is, therefore, significant.

Table 2. Spectral Comparison of Silane Treated (S) and Untreated (R) Co(II)-Montmortllonite Films

	% Transmission of Wavelengths (nanometers) Below														
	320	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
% TR:	25.0	37.0	51.0	59.5	65.5	72.0	75.0	78.0	80.0	81.5	78.5	71.0	66.0	61.0	57.0
% TS:	11.0	15.5	26.0	36.0	42.0	46.5	50.5	52.0	54.0	56.0	53.0	44.0	38.0	31.0	26.0
% T(R - S):	14.0	21.5	25.0	23.5	23.5	25.5	24.5	26.0	26.0	25.5	25.5	27.0	28.0	30.1	31.0
(%TS+25.1):	36.0	40.5	51.0	61.0	67.0	71.5	75.5	77.0	79.0	81.0	78.0	69.0	63.0	56.0	51.0
More Transparent:	S	S	-	S	S	R	S	R	R	R	R	R	R	R	R
|%TR - (%TS+25.1)|:	11.0	3.5	0.0	1.5	1.5	0.5	0.5	1.0	1.0	0.5	0.5	2.0	3.0	5.0	6.0
Difference Significant?:	yes yes													yes	yes

Mean and standard deviation of the %(T(R - S) values are 25.1 and 3.9, respectively.

Table 3. Spectral Comparison of Silane Treated (S) and Untreated (R) Cu(II)-Montmorillonite Films

	% Transmission of Wavelengths (nanometers) Below														
	320	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
% TR:	11.0	16.0	23.0	29.0	34.0	38.0	40.5	42.0	43.5	44.0	43.5	41.0	39.0	37.0	35.5
% TS:	1.0	1.0	2.0	6.0	13.0	19.5	25.5	30.5	35.0	38.0	38.0	35.0	32.0	28.0	24.0
% T(R - S):	10.0	15.0	21.0	23.0	21.0	18.5	15.0	11.5	8.5	6.0	5.5	6.0	7.0	9.0	11.5
(%TS+12.5):	13.5	13.5	14.5	18.5	25.5	32.0	38.0	43.0	47.5	50.5	50.5	47.5	44.5	40.5	36.5
More Transparent:	S	R	R	R	R	R	R	S	S	S	S	S	S	S	S
|%TR - (%TS+12.5)|:	2.5	2.5	8.5	10.5	8.5	6.0	2.5	1.0	4.0	6.5	7.0	6.5	5.5	3.5	1.0
Difference Significant?:			yes	yes	yes	yes				yes	yes	yes			

Mean and standard deviation of the %(T(R - S) values are 12.5 and 6.0, respectively.

Again confirming the eye, the differences between the Co-montmorillonite spectra are less significant than differences between the Cu-montmorillonite spectra (Tables 2 and 3, respectively). Untreated Co(II)-montmorillonite is generally more transparent above 650 nanometers and appears pink. Silane treated Co-clay is more transparent below 500 nanometers so that it appears more blue. The untreated Cu(II)-montmorillonite clay is significantly more transparent in the 400 to 600 nanometer range. This includes violet, indigo, blue, green, and yellow in the visible region. The clay appears a pastel green. The silane treated Cu(II)-montmorillonite is more transparent in the 750 to 900 nanometer region. This includes the red and near infra-red, the clay appearing yellow (Trujillo, 1962).

Combining x-ray and visible spectra information helps to explain the order of affinity the four homoionic montmorillonites exhibit for phenyltrichlorosilane expressed in their adsorption isotherms. The d(001) spacings of the benzene solvated clays suggest the preference Mg-montmorillonite has for the silane over Na-montmorillonite. The apparent additional success benzene has for swelling the interlamellar volume of Mg-montmorillonite may provide the silane with greater access to the clay's surface when compared to the Na-clay. Comparing the effects of benzene on the Na and Mg-clays, however, may not be quite so straightforward. Compared with water, benzene is a poor competitor for solvation sites on these metal cations. Probably, rather than swelling these clays, benzene may actually dehydrate them. If so, dehydration is more complete for Na-montmorillonite than its Mg counterpart, possibly due to the larger ionic radius and smaller positive charge of the Na cation. Enhanced silane adsorption by the Mg-clay may well be due to greater interlamellar volume and easier access to internal surfaces than in the Na clay. However, this is probably due to the inability of benzene to completely remove the hydration sheath of Mg^{+2}, rather than any ability benzene might have to solvate Mg^{+2} and swell the clay. Benzene's comparative success in dehydrating the Na cation probably relegates silane adsorption to external and edge surfaces of the Na-montmorillonite.

The x-ray data alone, however, do not explain why Cu-montmorillonite has a greater affinity for the silane than do the Mg or Co-clays. Hydrated Cu(II) ions exist primarily as hexaaquocopper(II) and, tetraaquocopper(II) cations (Clementz et al., 1973) when residing in the interlayer. Esr data, also indicate considerable variety in the stereochemistry of Cu(II) ions in the interlayers of Cu-smectites (Berkheiser and Mortland, 1975).

Cobalt and Cu-montmorillonites ostensibly possess greater affinity for phenyltrichlorosilane than their interlamellar volumes and similar surface areas would suggest, when compared with Mg-montmorillonite. Perhaps complex formation provides this additional affinity. Evidence exists, however, which rules out Cu or Co complexes forming with the phenyl group of the silane. First, the red copper benzene complex is not seen in the presence of the silane, under conditions which otherwise form it. This suggests the silane preferentially blocks the Cu from interacting with benzene. Foremost, however, is the fact that methyltrichlorosilane produces the same yellow Cu-bentonite as phenyltrichlorosilane but with no phenyl group present. Also, the 1426 cm^{-1} band of the phenyl group on the silane in solution, does not shift when the silane is observed residing at the clay surface; indicating little or no constraint on its vibration.

This information implies Cu-silane interaction is not mediated through the phenyl group. The "air dry" basal spacings for the Co and Cu-clays indicate a monolayer of water predominantly present, suggesting a four coordinate configuration. Four coordination is observed primarily in complexes containing large anions, such as chloride (Cl^-), or bulky neutral molecules. Perhaps a combination of these effects are involved if the silane-metal interactions are mediated through the chloride rather than the phenyl part of the silane.

The divalent metal-chloride anions, $CoCl_4^{-2}$ and $CuCl_4^{-2}$, are known to be blue and pale yellow respectively. These are, of course, the right colors for the silane treated, heat treated transition metal clays, but are almost surely not present as discrete entities in the interlayer due to electrostatic considerations. If discrete metal-chloride anionic complexes were responsible for these colors, they would surely be observed in solution rather than associated with the clay films. The solutions remained colorless. If, however, chlorides associated with the silane that remain bonded to Si, could successfully displace the coordinated water about the transition metal cations, a stable cationic complex might result with optical properties similar to the transition metal-chloride anions mentioned before. Being cationic, with no other competing cations, the complex (and its associated color) would remain at the clay surface. It would provide a source of uptake for the silane in addition to the large surfacial free energies presented by the clay surfaces. Small, highly charged ions form the most stable complexes. Also, complexes having central atoms with small ionic radii react more slowly than those having larger central ions. Copper(II), with an ionic radius of 0.69 Angstroms, should produce less labile complexes than Co(II), having an ionic radius of 0.78 Angstroms. In keeping with this argument, it should be mentioned that silane treated Co(II)-montmorillonite fades from blue to pink in less than an hour when removed from the 100C environment. In contrast, the yellow color of silane treated Cu(II)-montmorillonite, when removed from the 100C oven, persisted for several days before it eventually reverted to green. Both forms of these silane treated montmorillonites were allowed to sit, for over two months, exposed to the atmosphere. When placed in a 100C oven, with their untreated counterparts, the treated Cu(II)-clay changed from green to yellow and the treated Co(II)-clay changed from pink to blue. The untreated clays did not change color. This adds support to the idea that displacement of water by the silane is the reason for a color change and that the agent responsible for the color change is relatively stable in the interlayer.

SUMMARY AND CONCLUSIONS

The adsorption mechanisms responsible for the intercalation of organosilicon compounds in smectites are manifold. Of paramount importance are the effects of temperature, solvent system and counterions upon the rate, completeness, and processes that characterize these adsorption mechanisms.

When the adsorbate is a cation, as in the $Si(acac)_3^+$ system, ion exchange plays a significant role in the suite of reactions that lead to intercalates. The prominence of the ion exchange reaction is highly dependent upon the counterion occupying the exchange site and the solvent employed. When Co(II)-smectite is solvated with acetone, and $Si(acac)_3^+$ introduced, ion exchange is the principal path to intercalation, probably aided by chemisorption. Under similar conditions, the intercalation of $Si(acac)_3^+$ in Na or Mg-smectites proceeds with little or no counterion desorption. Here the intercalate forms via physical adsorption rather than ion exchange. Changing the counterion changes the mechanism of interaction. Changing the solvent also changes the mechanism. If water is used instead of acetone, physical adsorption and ion exchange compete simultaneously to produce the intercalate. Changing the solvent to water complicates the reaction dynamics further by introducing hydrolysis, and therefore, time dependent solution concentrations of organosilicon complex cation. The hydrolysis rate in solution is highly temperature dependent and somewhat pH dependent. Surface hydrolysis proceeds at a much slower rate due to surface stabilization of the cation as well as diffusion controlled mass action. Cationic hydrolysis products, i.e., protons, compete with both the organosilicon complex cations as well as the original counterions for cation exchange sites. Time dependent adsorbate concentrations prompted the development of a mathematical model to explain the atypical adsorption kinetics of the system. The fundamental equation is a function of the independent variable, time.

Complex adsorption is at its maximum initially in the Na system and at later times in the Mg and Co systems due to different diffusion rates associated with differing interlayer volumes. Supporting diffusion, with water as the solvent, are the relatively constant counterion desorption solution concentrations in the Na system contrasted with increasing counterion desorption over time in the Mg and Co systems.

When the adsorbate experiences no solvolytic degradation over time, typical adsorption isotherms may be reported, as was found with phenyltrichlorosilane in benzene. Still important, are the effects of solvent and specific counterions upon the rate, amount, and mechanism of adsorption. When the solvent is kept constant, differences in adsorption isotherms must be attributed to the counterions occupying the exchange sites of the homoionic montmorillonites studied. The amount of adsorption is, in increasing order; Na < Mg < Co(II) < Cu(II).

The important characteristics of the counterions, which control the amount of adsorption, are their ability to retain their hydration sheaths in the presence of a dehydrating solvent, and their electronic configurations. So, Na^+, and Mg^{++}, both having electronic configurations identical to the inert gas neon (Ne), differ in their abilities to retain hydration sheaths in the presence of benzene. This is primarily due to their differing ionic radii (0.95 and 0.65 Angstroms, respectively) and differing charge densities. The more labile hydration sheath of Na^+ cannot prevent the collapse of Na-montmorillonite to smaller interlayer volumes and more restricted internal surfaces than its Mg^{++} counterpart, as evidenced by x-ray diffraction data. The Mg-montmorillonite predictably adsorbs phenyltrichlorosilane more completely than does Na-montmorillonite. Both clays interact with the silane by physical adsorption.

The more complete intercalation exhibited by Co(II) and Cu(II)-montmorillonites is thought to arise from physical adsorption, aided by chemisorption. Under certain circumstances, the red Cu-benzene charge transfer complex is seen in the absence of phenyltrichlorosilane. Color changes associated with the Co and Cu-clays, coupled with esr data, imply d orbital interaction with the chlorides bonded to the Si atom in the silane. Dehydration of these homoionic clays by heating them to 100C produces a pink to blue color change in the Co(II)-montmorillonite and intensifies the green to yellow color change observed in Cu(II)-montmorillonite. Visible spectra confirm and quantitate these changes. The distortion of symmetric structures resulting from partially filled electronic energy levels (Jahn-Teller effects) are more easily manifested in the d^9 system of Cu(II) than in the d^7 system of Co(II). Chemisorption, then, is probably more significant in the Cu-clay than in the Co-clay.

The affinities of the four homoionic montmorillonites studied for phenyltrichlorosilane can be ranked according to their relative abilities to retain hydration sheaths, aided by their degree of d orbital interaction.

Of the two major intercalates studied, the Si(acac)$_3^+$ system appears more promising than the phenyltrichlorosilane system in the production of thermally stable pillared smectites.

The results of this work should be of utility in the conservation of prescious metals and in the more efficient and selective use of chemical feedstocks for the production of fertilizers, fuels, or indeed any product of a catalytic reaction, that might benefit from the introduction of inexpensive catalyst supports. Studies of this nature also allow us to become more proficient in our ability to modify the surfaces and fix the volumes of the clay interlayer, with implications toward the development of pollutant-specific fixation and degradation amendments for soils and sediments.

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