

STUDIES ON THE REACTIONS
BETWEEN
POLYVINYL ALCOHOL AND MONTMORILLONITE

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CHAPTER 1

INTRODUCTION

Polyvinyl alcohol-montmorillonite complexes on which the author intends to study belong to the third field of chemistry.

What is the third chemistry ?

As we all know, the science of chemistry can be divided into two branches, namely organic and inorganic chemistry. The organics go back to biological beginning and inorganics to minerals. They have made remarkable progressions in each field almost independently, but since the great German chemist Wöhler synthesized the first organic compound, urea, in 1828 the field of organic chemistry has spreaded acceleratively and millions of organic compounds are known, while there are a relatively few thousand inorganic compounds.

There are many differences between organic and inorganic compounds, starts from main species of constituent elements, rate of reactions, resistivity for heat, flexibility, elasticity, solubility and hardness etc.. If unions of organic and inorganic materials will be able to take place over wide range, numerous materials will be produced, which may be expected to have properties characteristic of both organic and inorganic compounds and so give rise to another large field of chemistry, which is the third field of chemistry.

One of the doors into the third field of chemistry has been opened by the appearance of organo-clay compounds in early 1930's.

Definition of the term " organo-clay "

Glaeser³⁰⁾ defined this term as follow " the term organo-clay is limited to the direct fixation of non-ionized molecules on clay by adsorption."

Nahin's definition⁷⁸⁾ is that " organo-clay are reaction products of specific clay minerals with specific organic molecules involving

the formation of chemical bonds. " Here very loosely associated aggregates of clay and organic materials are excluded from the chemical bonds, e.g. methane-montmorillonite at normal temperature and pressure.

Polyvinyl alcohol-montmorillonite complex is one of organo-clay in the latter conception.

What problems are treated in this field ?

The materials to be investigated in this field are mainly the unions of synthetic organic compounds and clay minerals which are clarified about their structures to some extent.

The importance of clay-organic interactions in industrial practices and the possibilities of producing materials with completely new or extensively modified properties have attracted considerable attentions to this field. And these organic materials-clay systems are studied by many scientists in many fields ; ceramic industry, paper makers, drilling fluids, lubricating greases, rubber industry, carriers of insecticides, adhesives, synthetic plastics, clarify of water and building materials etc..

On the other hand, since soil and lives appeared on our earth, organic materials-clay systems have been continued to exist in soil. By the interactions among clay, organic materials and microbes in soil, the primary particles such as clay minerals are aggregated to form the secondary particles which are the constituent units of soil aggregate. Such water stable aggregates influence plant growth by virtue of their relation to the maintenance of a porosity suitable for air, water and root movement. So the studies on soil-organic systems have extensively made in soil science, but these systems are remained almost unknown.

Needed studies on clay-synthetic organic compounds systems are ; to clarify the nature of the organic-clay bonds to more detail, to test the older methods of investigation and to construct new methods namely to construct the analytical chemistry of clay-organic systems.

Relating with the nature of the organic-clay bonds, the effects of the clay surface on infrared spectra of organic structures have already been studied in some detail, but the field is still very young and in need of many more answers than we now have. These problems present the chemist with a almost infinite variety of challenging objects.

By only developing those fundamental problems, the practical field will be opened before us.

Remaining those problems to be clarified in his mind, the author intends to carry out the experiments described below to gain some answers for the problems.

First of all, a brief review on the clay-organic complexes will be given in Chapter 2.

In Chapters 3 and 4, the interactions between polyvinyl alcohol and montmorillonite will be discussed phenomenally through the author's experiments.

The experiments on the polyvinyl alcohol-montmorillonite system will be developed into ontological stage in chapters 5, 6 and 8. Where some answers for the problems on the analytical chemistry of organo-clay will be given.

The mechanisms of bonding between polyvinyl alcohol and montmorillonite will be firstly certified with infrared spectra method by the author.

In Chapter 7, a proposal of new method for the determination of amount of adsorbed polymer to clay particles from water solution will be presented, which will throw an interesting doubt upon the routine centrifugal method.

Through these experiments, the autor's intention was fulfilled to some extent, and some results would contribute to the development of organo-clay chemistry.

CHAPTER 2

A REVIEW ON THE STUDIES ON CLAY-ORGANIC COMPLEXES

2.1 Clay-low molecular organic Complexes.

From early 1930's to 1940's, large amount of studies have been done on clay-organic systems. Here some of organic compounds used are picked up ; organic bases (nicotine, piperidine, amylamine, diamylamine, etc.⁹³⁾, piperidine, methylene blue, pyridine, aniline, brucine, β -naphthylamine, etc.²⁷⁾, several aromatic amines and heterocyclic compounds such as adenine, adenocine, guanine, guanocine, etc.⁴⁴⁾, amines (ethylene diamine, propylene diamine, hexamethylene diamine, diethylene triamine etc.) glycols (ethylene glycol, propylene glycol, ethoxy-trimethylene glycol.), ethanol, glycerol, sucrose, 1-4-dioxane etc.⁹⁾; monohydric alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 2-octanol, cyclohexanol etc.), polyhydric alcohols (ethylene glycol, 1-3-propanol, glycerol etc.), hydrocarbons (benzene, naphthalene etc.), chloroethanol, ethanediamine, acetone, nitromethane etc.⁶⁹⁾, aliphatic amines (butylamine, dodecylamine, octadecylamine etc.)⁵²⁾.

With such thorough coverage, one might ask what is left to be perspective about ? But since 1950's more systematical works have been conducted. For example, carbohydrate phosphates³²⁾, mononucleotides, nucleic acids³³⁾, amino acids⁹⁶⁾, aromatic organic compounds^{25), 26)}, alkyl amines^{3), 4)}, n-primary aliphatic amine salts¹⁴⁾, non-ionic aliphatic molecules⁴⁶⁾, ketones⁴⁷⁾, polyalcohols⁹⁸⁾ etc..

Indeed many organic compounds have been used to react with clays to form clay-organic compounds, while the species of clays used have been limited to two or three, especially montmorillonite has been used in much of those works,; for adsorption studies montmorillonite has great advantages over other clay minerals and most other absorbent, it has large surface area which is easily determined and

X-ray diffraction methods are used to study the organization of the adsorbed compounds.

X-ray observations and the knowledges about organic molecular size give the answers for the following three problems, 1) Whether inter-lamellar adsorption of compounds by montmorillonite occurs, 2) What orientation the adsorbed molecules take ? 3) How many organic molecular layers are formed ?

From Fourier analyses of organic complexes of montmorillonite the possible location of atoms of organic compounds can be determined with respect to the clay. Some attempts at such analyses have been made, but as yet the degree of resolution achieved is not sufficient to the atoms very precisely. Without Fourier analyses, the interpretation of the X-ray data must involve some degree of speculation.

In many instances some difficulties have been risen, namely in those complexes in which a single layer of organic molecules separates adjacent alumino-silicate lamellae the distance of separation is usually alightly less than the minimum dimension of the adsorbed molecules. This has been ascribed to the formation of C-H...O hydrogen bonds between the methylene groups and the oxygens of the clay surface^{10), 37), 69), 96)}, to keying of the molecules into the clay surface^{5), 29), 86)}, to general attractions between the surface and the adsorbed molecules⁴⁰⁾.

Differing from those molecules, when a molecule containing a long alkylchain of length about 30 Å gives rise to complexes with spacings of say 14 Å, 18 Å and another of about 40 Å. It is reasonable to assume that the first two refer to complexes in which the molecule is lying flat on the surface and the other to a complex where the adsorbed molecule is standing in a plane perpendicular to the surface^{60, 38)}. In many complexes of long-chain alkylammonium ions the alkylchains lie in a plane making a small angle with the clay surface¹⁰⁴⁾.

The methods, X-ray and Fourier analyses, do not of themselves

provide direct explanation relating to the interaction between organic molecules and clay. The limitation of X-ray diffraction studies has been complemented by infrared techniques, which give a useful knowledge about the interaction between organic molecules and clay, because when specific groups of an organic molecule interact with a surface on which the molecule is adsorbed, the movements of the atoms composing those groups will be modified, and this will result in a change in the frequency at which infrared radiation is absorbed. But infrared technique is not always almighty, it has also limitations. When the surface area of absorbent is small, and sufficient organic material does not get adsorbed to provide a measurable spectrum, this technique will lose its effectiveness in the study on adsorbing mechanisms.

Tensmeyer et al.⁹⁷⁾ compared the spectra of crystalline 2:5 hexanedione and 2:5:8 nonanetrione and these complexes with montmorillonite supported in KCl discs with those of their solutions in carbon tetrachloride. This they ascribed to weak C-H...O interaction of hydrogen bonding type in the adsorbed phase. If C-H...O bonding occurred, lowering of the C-H stretching frequencies should be observed, but this could not be observed¹²⁾. So the change in the deformation frequency might well be due to interactions within the electric field of the crystal of adsorbed layer other than C-H...O bonding.

French et al.^{26), 62), 65)} showed that shifts in the carbonyl group stretching frequency of adsorbed compound on montmorillonite are due to the formation of hydrogen bonding between them.

Suito et al.⁹⁵⁾ and Mitsui et al.⁶⁴⁾ have shown that the N-H frequencies of adsorbed amines were shifted in a way indicative of hydrogen bonding.

Considering the various properties of organo-clay complexes, it is also important to know the amount of adsorbed organic compounds on a certain clay. The system of montmorillonite and various amino compounds have been studied by determination of isotherms.

The adsorption isotherms obtained are Langmuir type²⁸⁾ and the initial slopes of the isotherms increase as the number of carbon atoms on the amino compounds increase, showing that the bonding strength is greater with the larger cations^{14), 39), 51), 71), 88), 99)}. So the amount of adsorbed molecules in initial stage have the relation with the molecular weight of adsorbent. If the number of carbon atoms dose not exceed 8, adsorption dose not proceed beyond the cation-exchange capacity of the clay, but for larger cations it is limited only the surface area of clay, this means that the adsorption of amino acid on clay occurs through two forces which act between them, one is electrostatic force and the other is van der Waals' force, the former, which is dominant in this case, relates with cation-exchange capacity, and the latter with surface area of the clay.

Adsorption as the cation takes place only below the isoelectric pH of the amino acids and is greater for the more basic ones^{89), 96)}. Very few studies of the adsorption of uncharged organic compounds from aqueous solution by montmorillonite have been reported.

Greenland^{37), 38)} showed that sugars were adsorbed, but only in very small amount unless the concentration was very high.

Ethylene glycol was not adsorbed in measurable amount from aqueous solution.¹¹⁾

Anionic materials such as tannates also adsorbed by clay¹⁰¹⁾.

Relating the amount of the adsorbed molecule with area of surface, it tried to determine the surface area of clay⁵⁷⁾.

Vermiculite, illite and micas react with long chain alkylammonium compounds to form interlamellar complexes^{102), 103), 104)}.

Kaolinite also react with alkylamines.^{40), 42)}

2.2 Clay-high molecular organic Complexes

The adsorbents high molecular compounds are proteins, synthetic organic polymers and soil organic matters, especially humic acids.

The adsorbents clays used are mainly montmorillonite and kaolinite.

X-ray diffraction methods have been used in the studies on proteins-montmorillonite complexes. It has been shown that globular proteins when adsorbed may uncoil, and give rise to interlamellar spacing of 5 to 10 Å, or may not uncoil or only partly do so, when interlamellar spacing of 30 Å and more are observed^{2), 72), 82), 96)}.

Like amino acids, it has been shown that the adsorption processes of proteins are both cationic exchange and physical adsorption^{2), 21), 27), 44), 96)}.

The amounts of proteins adsorbed are large up to 2.4 g/g of montmorillonite and limited by the surface area of clay, and not the number of charged sites on the surface^{2), 72)}.

Being adsorbed on interlamellar surfaces, proteins get resistibility against the degradation by microorganisms²²⁾.

Ruehrwein and Ward⁸⁴⁾ reported that cationic organic polymer are adsorbed by montmorillonite through the same adsorption process as proteins are.

It have been reported that polyanions did not be adsorbed in the interlamellar regions of montmorillonite^{1), 17), 43), 48), 84)}, so edge surface of clay becomes to have more important meaning in the adsorption of anionic compounds. The adsorption of anionic materials has therefore been studied in more detail with kaolinite.

Kaolinites have important structural differences to the mica-type layer lattice silicates; one basal face of the crystal is silicate sheet but the other is a gibbsite sheet. Several observations support that the edges of the kaolinite carries positive charge.

Thiessen¹⁰⁰⁾ showed that negatively charged gold particles were adsorbed by the edges of kaolinite through electron micrograph.

Schofield et al.⁸⁷⁾ and Quirk⁸³⁾ showed also the edges of kaolinite lattice become positively charged at low pH. It may be expected that negatively charged compounds are readily adsorbed on the positively charged edges of clays. And this system of organic polymer-kaolinite has received considerable attention relating with soil

conditioners.

In the study on this system, instead of X-ray methods, colloid chemical techniques such as flocculation and deflocculation of clay suspension with addition of organic matter, are applied.

The positive charges at edges enable it to form termed " peripheral " complexes with anionic compounds^{17) 73), 74), 75), 76)}.

Although the pH at which most adsorption occurs is where the kaolinite is positively charged, Michaels et al.⁷⁵⁾ and Kita⁶¹⁾ considered that the pH effect is due to its influence on polymer configuration, which plays important role in the physical adsorption of polymer.

Mortensen⁷⁷⁾ has shown that the adsorption of anionic polymers is greater in presence of salts, or of cations which decrease the zeta potential of the polymer and the clay, for electrostatic repulsion between clay and polymer is reduced so that a closer approach is possible, and physical interactions can become important, he also considered that as well as reducing the zeta potential, the presence of polyvalent cations enhanced anion adsorption on kaolinite by formation of bridge linkages.

Non-ionic polymers are adsorbed in large amount and strongly retained^{17), 41), 68), 85)}.

The exchangeable cation influences on the dispersion of the clay and the accessibility of interlamellar surfaces. Most of the works reported has been with hydroxylic compounds and it has generally been suggested the compounds are hydrogen-bonded to the clay surface, but no satisfactory evidence to establish this has been presented.

Most of the studies of adsorption of uncharged polymers have shown that once adsorbed it is extremely difficult to desorb the polymer molecules^{20), 41), 79), 91)}. It is to be expected when adsorption is due to a large number of weak binding points, since although any one segment of the polymer may be readily desorbed, it is improbable that all segments will be desorbed simultaneously,

the condition necessary if the polymer is to be desorbed from clay particle.

From detailed theoretical treatment, Silberberg⁹⁰⁾ 91) has shown that the strong adsorption by multiple weak surface-segment interactions can be accounted for very satisfactorily and that theory also predicts irreversibility and collapse of the polymer to the surface, provided the polymer molecule is sufficiently flexible. The physical adsorption would play main role in the adsorption of non-ionic polymer.

One field of organo-clay systems exists in soil, but the interaction between clays and organic materials in soil is a difficult to investigate. Not only are there many uncertainties still remaining regarding the constitution of the bulk of the organic material that is present, but precise condition of the surface with which union takes place is seldom known. These surfaces may be the relatively simple ones indicated by the known structures of clay minerals, but they may also be surfaces of amorphous or poorly crystallized oxides or hydroxides of silicon, aluminium and iron, present as such or as encrustations on the surfaces of clay minerals. The interaction on the surface of clay minerals occurs in a multicomponent system which is a further complication of the phenomenon.

Very simplified systems have been investigated also in this field, for example, an extracted organic materials which are relatively compact, negatively charged spheres. So it is expected that they will be repelled from the largely negatively charged surfaces, and presumably they are held by positively charged sites on the clay particles.

Flaig and Beutelspacher²⁴⁾ considered that electron micrographs of mixtures of montmorillonite and humic acids show that an association between humic acids and montmorillonite occurs only through the intermediary of aluminium or iron oxides.

In the presence of polyvalent cations, larger amounts of humic

acids are adsorbed by clay minerals^{23), 53), 56)} which is explained in terms of formation of bridge-linkages with polyvalent cations.

Beutelspacher⁷⁾ suggested from his electron micrographs that humic acids are attached only to the edges of kaolinite crystals, as might be expected.

The soil polysaccharide readily formed an interlamellar complexes with montmorillonite^{15), 37)}, this strong adsorption is type of behaviour that would be predicted for large, linear, uncharged molecules.

Although some understanding of the interaction between clays and defined organic compounds has now been obtained, an appreciation of the mechanisms responsible for the formation of the natural clay-organic complex is hindered by inadequate knowledge of the structure and composition of soil organic compounds.

DISPERSION AND FLOCCULATION OF CLAY PARTICLES IN
WATER SUSPENSION AS AFFECTED BY POLYVINYL ALCOHOLS

A system in which small amount of clay particles are dispersed in large amounts of water, shows the properties of both sol and suspension. These two properties of such system seems to be due to wide distribution of the particle size of the clay, for parts of particles with small diameter do not settle to the bottom within a considerable time, so these particles have the characters of sol, while other parts of dispersant with large particle size settle comparatively rapidly so these particles have the characters of suspension. Of course the distinction between a sol and a suspension is entirely arbitrary.

The clay-water system used in this experiment will be called a clay suspension according to the customs.

Here in this chapter, the author intends to clarify the interaction between clay particles suspended in water and polyvinyl alcohol molecules through the phenomena of dispersion and flocculation of clay particles in the system.

Relative to the above intention, it will be useful to give some reviews about clay particles in water. Some works about the existing state of montmorillonite particles in water suspension were presented.

Hight⁴⁵⁾ said that sodium-montmorillonite is dispersed to unit layer in its water suspension through his experiments conducted by low angle X-ray diffraction method.

On the other hand, M'Ewen⁷⁰⁾ suggested that sodium-montmorillonite particles make a libbon like edge to edge aggregate in its water suspension.

Thus the knowledges about the existing state of sodium-montmorillonite in water is yet ambiguous. Nevertheless, there is an

unanimity among different investigators that sodium-montmorillonite disperses to unit layer in its water suspension, in other words, the kinetic unit of sodium-montmorillonite in water is unit layer of montmorillonite. It is also an important problem to clarify the existing state of montmorillonite in water.

The forces acting among dispersed clay particles suspended in water will be considered, for they will have an intimate relations with the phenomena of dispersion and flocculation of clay particles in the system.

The dispersed state of clay particles is largely attributed to the repulsive force of an electrical nature, i.e. the formation of electric double layer around clay particle. When two particles approach each other in suspension owing to their Brownian motion, electric double layers of these two particles begin to interfere and separate them again, but if attractive force is operative and superiour to the repulsive force, the approached particles would be aggregated to make a larger particle.

As mentioned above, other forces acting among clay particles are interparticle attractive forces such as van der Waals' force and electrostatic attractive force.

The phenomena of flocculation and deflocculation of the clay suspension are decided by the superiority of inferiority between these two, repulsive and attractive, forces. For example, if small amount of inorganic salt are added to clay suspension, the electric double layer around clay particle would be compressed, consequently two particles could approach nearer each other until these compressed electric double layers begin to interfere, and this condition might make the attractive force to be superiour to repulsive force, and bring particles to aggregated state.

Besides inorganic salts, there is another way to break up the relation of those opposite forces in water, it is the addition of organic chemicals to the suspension of clay.

With respect to this point, natural organic polymers such as starch and gelatine have flocculating power for clay suspension, and in recent year, chain-like synthetic organic polymers have used for flocculating agents for clay particles.

These polymers are supposed to build the bridge between clay particles and flocculate them. Mechanisms of bonding between clay particles and polymer molecules presented are physical adsorption, hydrogen bonding and salt exchanging type bonding etc.. It is also presented that generally polymer molecules are adsorbed onto clay surface firmly.

Here another force may be added to the interparticles force, not in precise meaning, namely the force to form polymer bridge between clay particles.

In this chapter, various conditions which are supposed to affect on the phenomena of flocculation and dispersion of clay suspension by polyvinyl alcohol will be discussed.

Those conditions are thought to be the effects of concentration of the clay suspension, effects of degree of polymerization of polyvinyl alcohol, effects of pH of the medium of the clay suspension, effects of the exchangeable cations of the clay and effects of addition of inorganic salts.

Behaviours of the calcium-montmorillonite in water will be discussed in connection with its existing state.

Besides flocculation-deflocculation experiment, X-ray diffraction techniques were employed for studying the adsorption of polyvinyl alcohol molecules onto intercrystalline surface of montmorillonite.

Results in this chapter will have an important significance in utilizing to the industries of water cleaning, soil conditioning in agriculture and civil engineering etc..

3.1 Materials and methods

Materials

Clay mineral used in this experiment was Bentonite produced in

Gunma Prefecture and sold at market as Silicalight A in commercial name. Results of X-ray analyses and chemical analyses show that this clay includes montmorillonite and cristobalite as two main clay minerals and dominant exchangeable cation of the clay is sodium ion. This clay sample was designated as Na-Bent through this experiment.

Various clay samples were prepared from Na-Bent. Firstly the exchangeable cation of Na-Bent was exchanged for calcium ion to gain calcium-Bentonite (Ca-Bent). Secondary in order to gain montmorillonite rich clay, clay particles less than $2\ \mu$ in its diameter were separated from Na-Bent. Results of X-ray and chemical analyses show that this clay sample is almost sodium-montmorillonite only, so this clay sample was designated as Na-Mont. The exchangeable cation of Na-Mont was exchanged for potassium, magnesium and calcium ion to get potassium-montmorillonite (K-Mont), magnesium-montmorillonite (Mg-Mont) and calcium-montmorillonite (Ca-Mont), respectively.

Organic polymers used were polyvinyl alcohol samples which are given in Table 3.1.

Table 3.1 Polyvinyl alcohol (PVA) samples used

PVA	D.P	D.S (mol %)	PVA	D.P	D.S (mol %)
PVA-1	300	88	PVA-1'	300	98
PVA-2	500	88	PVA-2'	500	98
PVA-3	1700	88	PVA-3'	1700	98
PVA-4	2700	88	PVA-4'	2700	98

where D.P : degree of polymerization

D.S : degree of saponification

From those clay samples and polymers, appropriate couple were used in each experiment, combination of them will be given in each place.

Experimental methods

Measurement of the degree of the flocculation of a suspension
In a series of test tubes, increasing amounts of polymer solution were added to a certain amount of clay suspension. The contents of the test tubes were mixed by shaking, and the tubes allowed to stand for an arbitrary chosen time at constant temperature. At the end of this period, the definite amount of supernatant solution was pipetted out from the definite depth of a test tube. The supernatant pipetted out was diluted and its turbidity was measured by using Beckmann type spectrophotometer. The wave length used was 500 - 550 mμ. Turbidity of a sample was expressed as the relative value against the turbidity of completely dispersed sample, in which no polymer was added. An example of the turbidity expression is given by following equation ;

$$\text{Relative turbidity of sample A} = \frac{\text{Turbidity of sample A}}{\text{Turbidity of sample S}} \cdot 100$$

where sample S is the sample in which no polymer is added.

Relative turbidity is supposed to give the relative numbers of the clay particles in the supernatant, which is inversely proportional to the degree of the flocculation of the system.

Experiment was carried out on doublet or triplet samples. The standing time and other treatment done on clay sample before the addition of polymer will be mentioned in each place.

Measurement of the pH of the medium

The pH of the sample was measured by Hitachi model of pH meter with glass electrode.

X-ray diffraction analysis

After pipetting out the supernatant for turbidity measurement, the remained content of test tube was dried on a glass plate and the oriented sample was offered to X-ray analysis. Before offering to X-ray analysis, the oriented sample was equilibrated with 50 % relative humidity at room temperature for more than 48 hours. X-ray

analyses of samples were conducted by using Norelco X-ray diffractometer. General conditions of experiments employed are given in Table 3.2

Table 3.2 Experimental conditions of X-ray analyses

Target	Cu
Filament current	15 amp.
Filament voltage	40 kV.
Filter	Ni
Scale factor	8 - 4
Multiplier	1
Time constant	4 - 2 sec
Scanning speed	1°/min.

3.2 Results and discussions

i. Effects of the concentration of clay suspension

Mechanism of the flocculation and dispersion of the clay suspension as affected by polyvinyl alcohol is supposed to be different from that phenomena of clay suspension with salt addition, in the latter case the phenomena of flocculation and deflocculation of the clay suspension are decided by salt concentration and not by the concentration of the clay suspension, while as mentioned before polymer molecules are supposed to construct bridges among particles to flocculate them, consequently distance between two particles seems to have an important significance on the flocculation-deflocculation phenomenon of the system of clay-polymer-water.

It is necessary to decide the optimum clay concentration for this experiment. Three clay suspensions were employed for this purpose.

Polymer used was PVA-3 and the standing time of the test tube before turbidity measurement was 20 hours at 30°C.

The results of turbidity measurement are illustrated in Figure 3.1.

The mode of curve 1 shows clear difference from these of other

curves. Flocculation phenomenon could not be observed in curve 1, while flocculation-deflocculation of clay particles were observed in other two systems. One of the reasons why flocculation of clay particles did not be occurred in system 1 is supposed to be the large interparticle distance in system 1 and this large interparticle distance seems to make it impossible to form bridges of polymer molecule between dispersed clay particles.

On the other hand, in curves 2 and 3 clay particles are flocculated by the increasing amount of PVA added and flocculation of the systems reached to maximum point then again the systems begin to disperse with further addition of polymer. The polymer added clay ratio at maximum flocculation are 8 % in both 2 and 3. This is the most conspicuous feature in these systems and it suggests the existance of an intimate relationship between flocculation-deflocculation phenomena and the surface available to polymer adsorption.

0.5 % clay suspension will be employed in most of experiments, for there was an inconvenience for pipetting out of the supernatant in higher clay concentration, because of large amount of the flocs made. But the clay concentration of 0.1 % will be employed in the system of Mont-PVA-salt solution.

Of course, it is possible to measure the degree of flocculation or dispersion of the system of clay-polymer-water over wide range of clay concentration from the flow properties of the system, but these methods did not be employed in this experiment.

ii. Effects of the degree of polymerization of polyvinyl alcohol
Flocculation-deflocculation experiment was conducted by using PVA-2, PVA-4 and Na-Bent.

In Figure 3.2 are illustrated turbidity vs. the amounts of polymer added for three systems.

In the first place, the same tendency in three curves are observed, i.e. the maximum flocculation of these systems are observed when 8 % of PVA is added to the clay, especially the form of curves 2 and 3

are almost the same, which suggests the mechanism of flocculation of the clay particles by PVA would be different from that by inorganic salt.

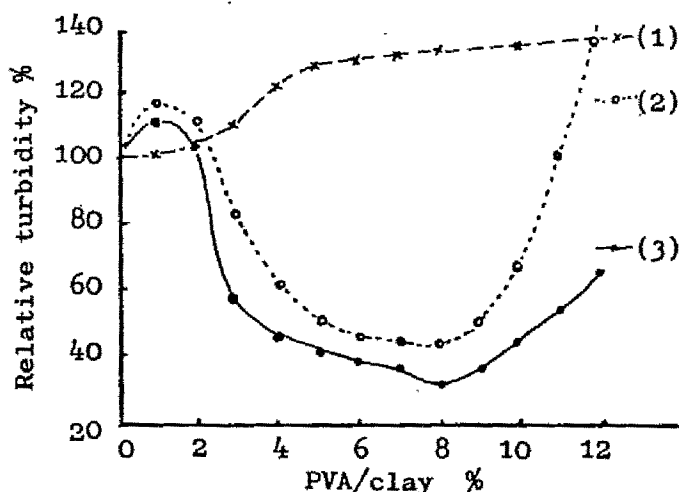


Figure 3.1 Results of turbidity measurement of PVA-3 Na-Bent system. (Effects of clay concentration) where the concentrations of clay suspensions giving curves 1, 2 and 3 are 0.1, 0.5 and 1 %, respectively.

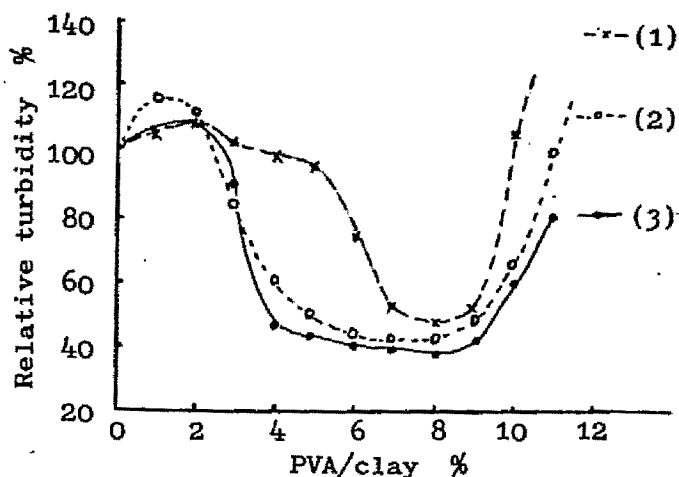


Figure 3.2 Effects of D.P. of PVA where D.P. of PVA of systems giving curves 1, 2 and 3 are 500, 1700 and 2700, respectively.

On the other hand, there are some differences in three curves, i.e. the amount of polymer added to clay at the beginning of flocculation of these system are different in curves 2, 3 and curve 1. Curves 2 and 3 begin to flocculate when 3 % of polymer are added, while curve 1 begins to flocculate when 5 % of PVA is added to the clay.

It is inferred from these facts that the active part of polymer molecules for the flocculation phenomenon would be protruding parts of PVA molecule adsorbed onto clay surface. Because the higher the degree of polymerization of the polymer, the longer the parts of the polymer protruding into medium become, so it seems to promote the formation of polymer bridge between particles into flocculate.

X-ray diffraction analyses of the complexes formed with polymer of various degree of polymerization were conducted so as to examine those considerations about flocculation mechanisms.

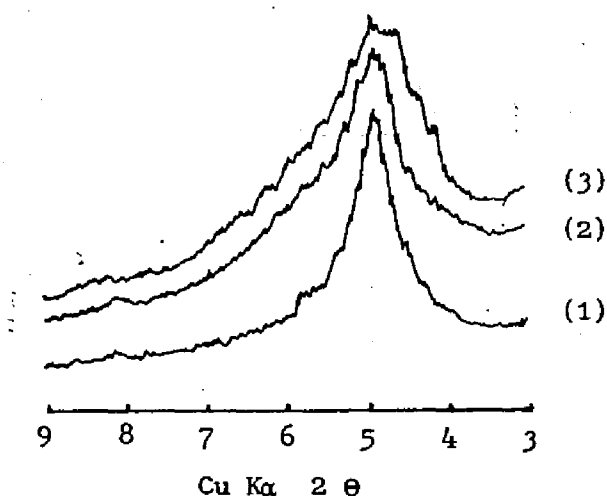


Figure 3.3 X-ray diffraction patterns for complexes where D.P of PVA in systems presenting curves 1, 2 and 3 are 500, 1700 and 2700, respectively. The amounts of polymer added to clay was 15 % in all samples.

A shoulder is observed at 5° in curve 3 and there any similar shoulders do not be observed in other two curves. It is clearly said that the higher the degree of polymerization of polymer, the lower the degree of the orientation of polymer molecules adsorbed onto inter-crystalline surface of montmorillonite, and this also suggests that the higher the degree of polymerization of polymer, the longer the parts of polymer molecules protruding into medium become.

Mechanisms of the flocculation of the clay particles by PVA are considered to be the following two ; 1) Polyvinyl alcohol molecules adsorbed onto clay surface make that parts of surface hydrophobic, which would hinder the formation of electric double layer, so two particles could approach nearer each other, and 2) The formation of interparticles bridge by polyvinyl alcohol molecule, and this would play main role in the flocculation phenomenon.

The particles which is settled into the bottom for a definite time intervals must to have the particle size of more than a definite diameter and this particle would be formed by the mechanism 2. Comparing these two mechanisms, the mechanism 2 seems to be more important for the flocculating process. And this consideration is reasonable when we remember the phenomenon presented in curve 1 in Figure 3.1.

When less than three percent of PVA was added to the system, more than 100 % of relative turbidity was observed. This high relative turbidity is considered to be the increase in particle number which would be brought by changing in the specific gravity of clay particle with polymer molecules, of course this particle would settle later, consequently the number of particle in the supernatant would increase.

iii. Effects of pH of the medium

As mentioned in the preceeding experiment, the force acting to make the clay particles dispersive in its water suspension, is the repulsive force between particles which is attributed to the zeta potential of hydrated clay particles. This zeta potential will be changed with

changing in pH of the medium, so the valance between repulsive and attractive forces may be altered by pH values of the systems.

Here the flocculation-deflocculation of the system of clay-PVA-3 with various pH will be discussed.

pH of the clay suspension was adjusted by HCl and after standing the clay suspension for 24 hours, increasing amounts of polymer solution were added. Other procedures were the same those adopted in the former paragraph.

The standard of turbidity was taken the turbidity of the sample in which no polymer was added and its pH was 7.05. The results were presented as the relative value for the standard one.

Some of the relationships among relative turbidity of the system, amounts of PVA added to clay and the pH of the medium are illustrated in Figure 3.4.

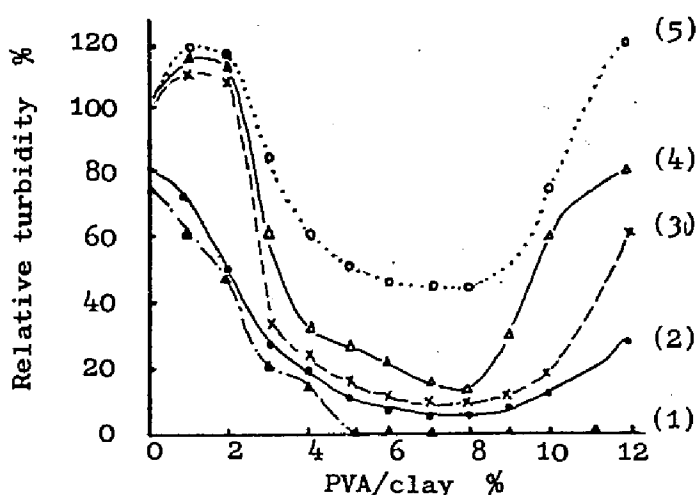


Figure 3.4 Effects of the pH of systems of flocculating behaviour of PVA-3-Na-Bent-water systems where pH of systems giving curves 1,2,3,4, and 5 are 4.20, 5.20, 5.90, 7.05 and 9.50, respectively.

Especially it is noteworthy that the lower the pH of the medium, the higher the flocculation of system becomes. This tendency of curve suggests that repulsive force acting among particles would be shorten and this condition would make it easy to construct inter-particle bridges of polyvinyl alcohol molecules. But it is also noteworthy that the maximum flocculation of these systems are observed when 8 % of PVA is added independently of flocculation in lower pH region. This fact could be explained adequately by assuming that the surface area available to the adsorption of polymer molecules remains unchanged over these pH region.

With intention to clarify this inference, X-ray diffraction analyses for the several complexes prepared under different hydrogen ion concentration were conducted.

Obtained X-ray diffraction diagrams are illustrated in Figures 3.5 and 3.6.

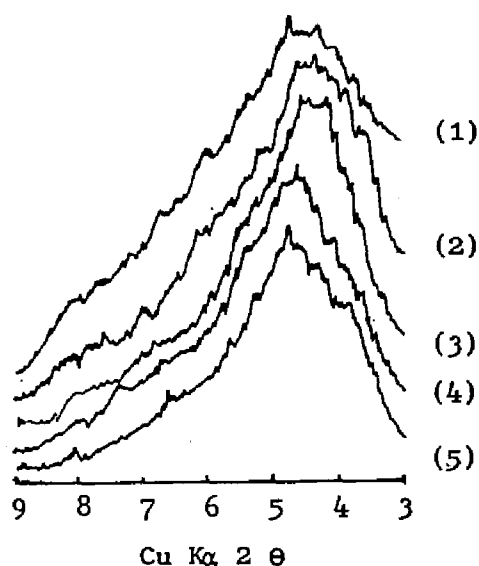


Figure 3.5 X-ray diffraction patterns for complexes formed under different pH where pH of the systems giving curves 1,2,3,4. and 5 are 1.20, 1.50, 1.90, 2.30 and 3.25, respectively, amounts of PVA added to clay is 15 % in every sample.

Under pH values of systems presented in Figure 3.5, clay particles were flocculated without addition of PVA.

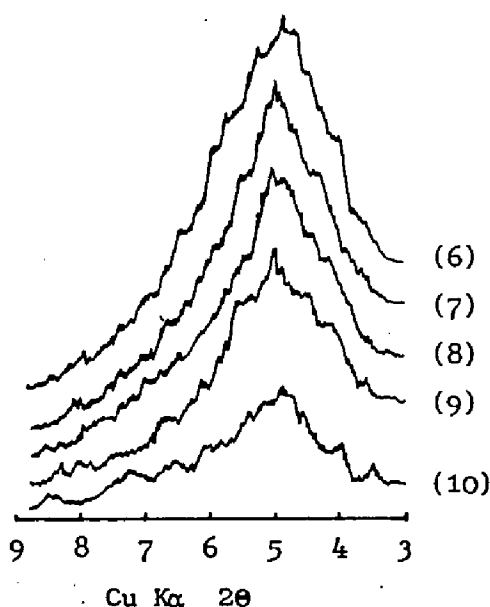


Figure 3.6 X-ray diffraction patterns of complexes formed under different pH of the systems where pH of systems giving patterns 6,7,8,9 and 10 are 5.50, 6.45, 7.05, 8.10 and 12.20, respectively, and 15 % of PVA is added to clay.

Only the system of 10 was flocculated without PVA addition.

The original basal spacing of montmorillonite is 12.3 Å under the condition employed in this experiment. So when two molecular layers of PVA are formed between intercrystalline lattice of montmorillonite, its basal spacing became 17.5 to 18.5 Å. Figure 3.5 suggests that two layers of PVA molecules are formed between intercrystalline surface of montmorillonite, and these facts mean that the distances of the intercrystalline lattice of montmorillonite before polymer addition would be more than 300 Å. 300 Å is the molecular size of PVA-3 in water solution.

In spite of the resemblance of the modes of these curves, some

differences are observed among them. The degree of orientation of polymer molecules adsorbed onto intercrystalline surface becomes lower in the samples formed under lower pH value, which suggests that the distance of intercrystalline lattice of montmorillonite would be shortened to some extent by interparticles flocculation.

Curves in Figure 3.6 show almost the same mode among them, i.e. two layers of polymer molecules are formed in inner surface of montmorillonite.

Here two steps of flocculation of montmorillonite particles are deduced from these data, i.e. flocculation of interparticles which occurred in the first step, and flocculation of intercrystalline lattice.

It should be mentioned that the reaction between polyvinyl alcohol and montmorillonite was carried out under the condition of clay concentration of 0.5 %, and if the concentration of clay suspension is different, the effects of pH on the formation of PVA-Mont interlamellar complexes might be different. And it is inferred that the higher the concentration of clay suspension, the larger the effects of pH on the formation of PVA-Mont interlamellar complexes becomes.

iv. Effects of exchangeable cation of clay

Barshard⁶⁾ studied about effect of exchangeable cations on the formation of water layers in the intercrystalline of montmorillonite and reported that number of water molecular layer is the largest in sodium-montmorillonite under the circumstance of constant relative humidity.

Norrish studied about the degree of intercrystalline expansion of montmorillonite in dilute salt solution where he said that calcium-montmorillonite expanded to about 20 Å in its basal spacing in water suspension.⁸¹⁾

As mentioned before, the flocculation-deflocculation of clay suspension with polymer molecule is decided by the surface area available to polymer adsorption. Considering from the behaviours of

montmorillonite with various exchangeable cations, the surface available to polymer adsorption is supposed to be different from each other by its exchangeable cation.

A purpose of the experiment in this paragraph is in clarifying the effects of cations of montmorillonite on the flocculation-de-flocculation phenomena of clay-PVA-water system.

Clay samples used in this experiment were Na-Bent, Ca-Bent, Na-Mont, Ca-Mont, K-Mont and Mg-Mont. Polymer used was PVA-3. Procedure of experiment was the same as given in the former paragraph.

The results of measurement of relative turbidity of systems of PVA-Bent are presented in Figure 3.7.

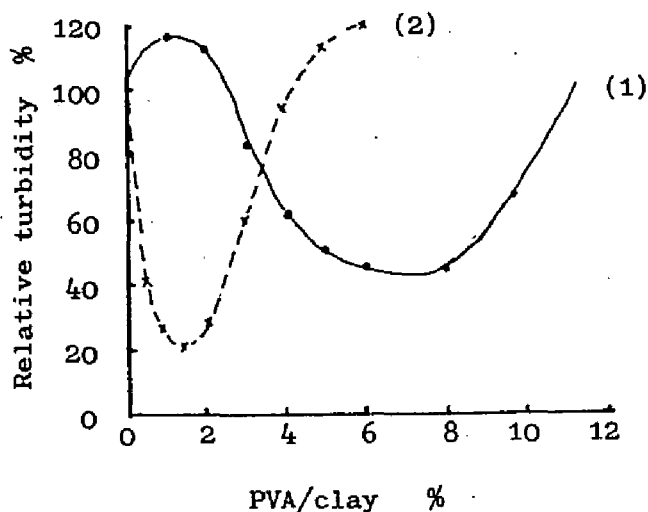


Figure 3.7 Effects of exchangeable cations on the flocculation of PVA-Bent systems.
where exchangeable cations of the systems giving curves 1 and 2 are sodium and calcium ion, respectively

The most conspicuous feature in these curves is the difference of

the maximum flocculating points, namely in the system of Na-Bent, when 8 % of PVA is added to clay the maximum flocculation is observed while only 1.5 % of PVA is enough to flocculate Ca-Bent system. This difference in maximum flocculation will be discussed from the results of X-ray analyses of these samples.

In Figures 3.8 and 3.9 are illustrated the X-ray diffraction patterns of complexes of PVA-Na-Bent and PVA-Ca-Bent, respectively.

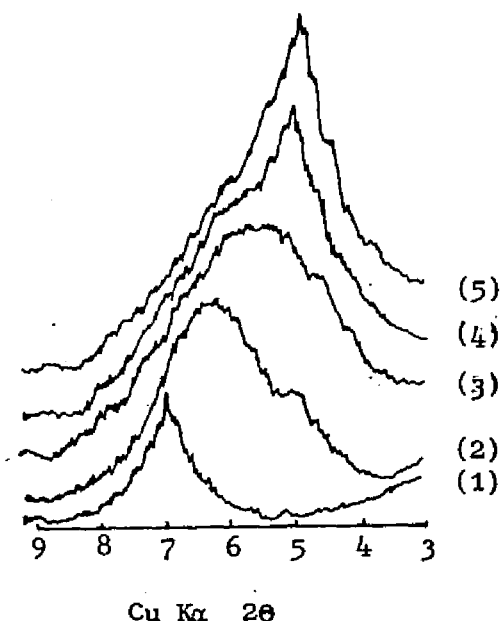


Figure 3.8 X-ray diffraction diagrams of PVA-Na-Bent complex where amounts of PVA added to clay of complexes giving curves 1,2,3,4 and 5 are 0, 5, 10, 15 and 20 %, respectively.

These diffraction patterns show that the basal spacing of montmorillonite increases from 12.3 to 18.5 Å with the increase of the amounts of polymer added to clay and this fact suggests that polyvinyl alcohol molecules might be adsorbed onto intercrystalline surface of montmorillonite.

The remarkable changes in the basal spacing of montmorillonite do not be observed in these curves in Figure 3.9 in spite of the increase

of amount of polymer added. The distance of (001) spacing of montmorillonite in these samples is 15 Å and this value shows that two molecular layers of PVA did not be formed in intercrystalline lattice of montmorillonite.

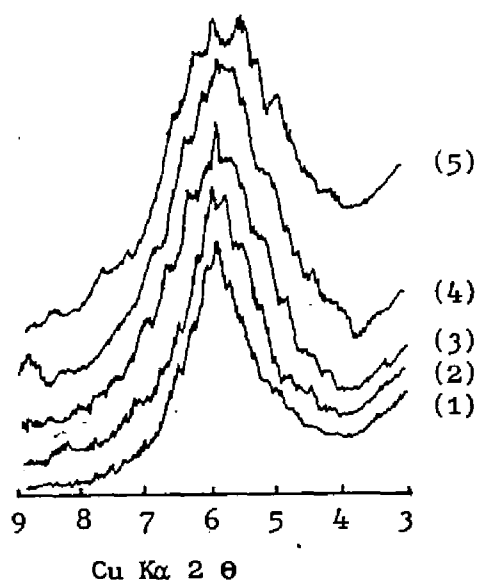


Figure 3.9 X-ray diffraction patterns of PVA-Ca-Bent complex where amounts of PVA added to clay in curves 1,2,3, 4 and 5 are 0, 5, 10, 15 and 20 %, respectively.

But more detail observation of the form of these diffraction patterns, suggests that the higher the percentage of PVA added to clay, the broader the shape of peak becomes. It is inferred from this tendency that only one molecular layer of PVA might be formed between intercrystalline entrance of montmorillonite. Thus difference in flocculating points is attributed to the surface area available to polymer adsorption.

Results of measurement of relative turbidity of system of PVA-Mont are illustrated in Figure 3.10.

The analogous difference in the maximum flocculation of the systems are observed in curves in Figure 3.10.

Especially it is noteworthy that curve 2 in Figure 3.10 shows two flocculating regions. From this curve, it is inferred that K-Mont would be consisted of clay particles with various characters.

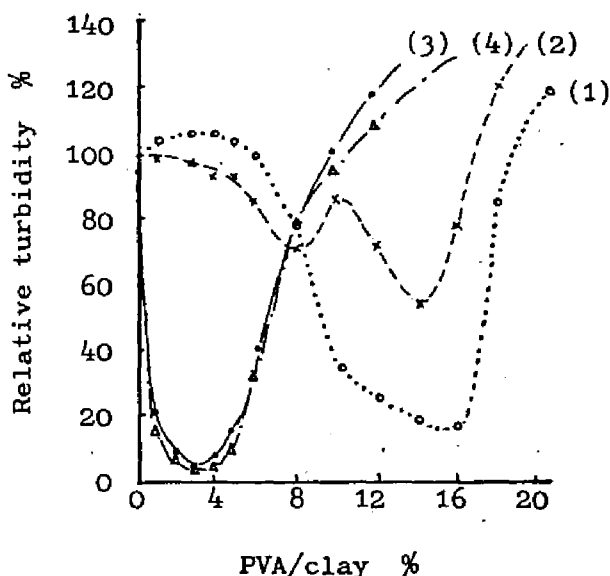


Figure 3.10 Effects of exchangeable cations of Mont.

where exchangeable cations of the Mont giving curves 1,2,3 and 4 are sodium, potassium, magnesium and calcium, respectively.

The difference in the points of the maximum flocculation of the systems will be discussed by illustrating the results of X-ray diffraction patterns of these samples.

X-ray diffraction patterns of these samples are illustrated in Figures 3.11, 3.12, 3.13, and 3.14.

Diffraction patterns in Figure 3.11 show the analogous forms to those in Figure 3.8, i.e. a gradual increase of the basal spacing is observed with increasing of PVA added. When 5 % of PVA was added to the clay, mono-molecular layer of polymer was formed in intercrystalline lattice of montmorillonite, in this case the basal spacing of montmorillonite becomes about 14.5 Å. When 10 % of PVA

was added to clay, this basal spacing of montmorillonite is changed to about 17.5 to 18.5 Å, and when 15 % of PVA was added to clay, only the complex in which two molecular layers of PVA are adsorbed onto intercrystalline lattice of montmorillonite is observed. When 50 % of polymer was added to clay, multi-layers of polymer molecules were adsorbed on inner surface of montmorillonite.

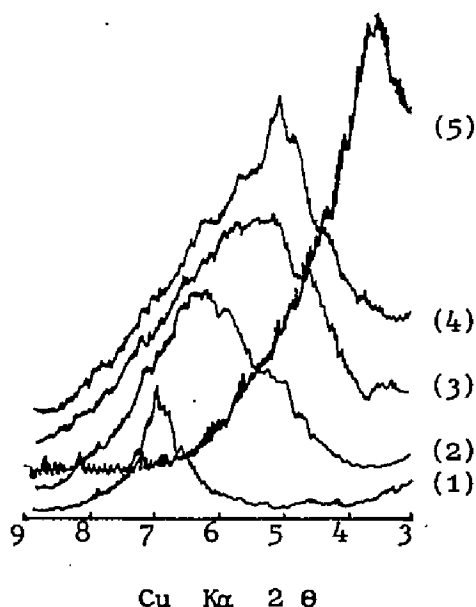


Figure 3.11 X-ray diffraction patterns of PVA-Na-Mont complex.

where amounts of PVA added to clay of complexes giving diffraction patterns 1, 2, 3, 4 and 5 are 0, 5, 10, 15 and 50 %, respectively.

The most remarkable fact in the diagrams in Figure 3.12 is that a stepwise adsorption of polymer observed in curves in Figure 3.11 does not be observed in these curves. A broad shoulder is observed when 5 % of PVA was added to clay.

It is inferred from the mode of curves in Figure 3.12 that K-Mont consists of non-expansible parts like illite and easily expansible parts like sodium-montmorillonite and the intermediate parts of them.

The peculiar behaviour of K-Mont-PVA-3-water system would be attributed to the variety of the constituting members of K-Mont.

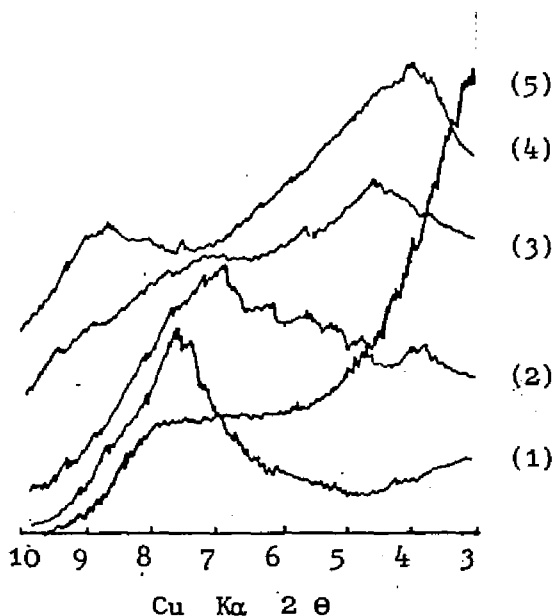


Figure 3.12 X-ray diffraction patterns of PVA-K-Mont complex where amounts of PVA added to clay of complexes giving patterns 1, 2, 3, 4 and 5 are 0, 5, 10, 15 and 50 %, respectively.

The resemblance in the mode of curves in Figures 3.13 and 3.14 is fully coincident with that in flocculating behaviours of two systems.

A small difference in the maximum flocculating points of those two systems may be attributed to the existence of some expansible particles in Mg-Mont, i.e. when 8 % of polymer was added to clay, somewhat indistinct diffraction peak appears at 5° . But two layers of PVA molecules could not be observed in intercrystalline lattice of the principal parts of montmorillonite.

Almost no difference in the basal spacing of montmorillonite is observed with the increase of polymer added to clay in curves of Figure 3.14. Evidently in every case, two layers of polymer molecules did not be adsorbed in intercrystalline lattice of Ca-Mont,

but there is no evidence to deny the possibility that adsorption of mono-layer of PVA molecules in inner surface of montmorillonite might be occurred.

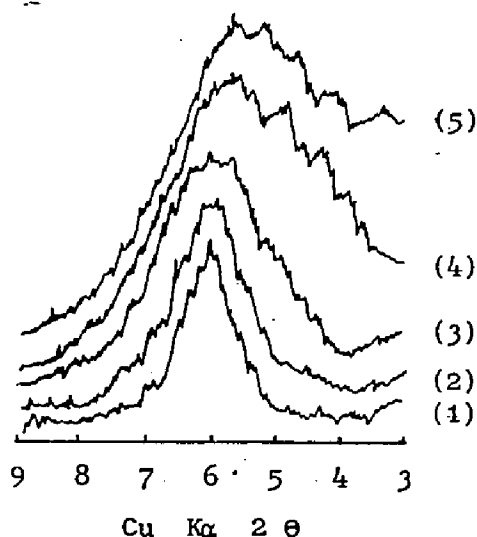


Figure 3.13 X-ray diffraction patterns of PVA-Mg-Mont complex.
where amounts of PVA added to clay of curves 1,2, 3,4 and 5 are 0, 4, 8, 15 and 50 %, respectively.

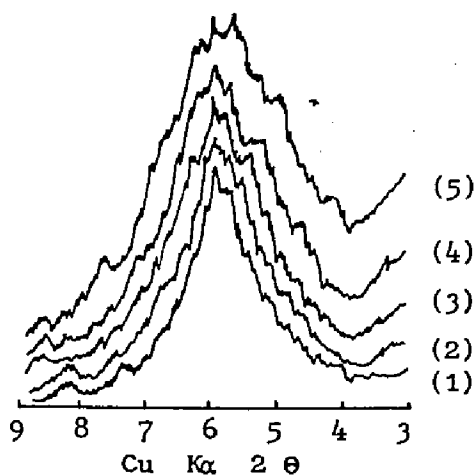


Figure 3.14 X-ray diffraction patterns of PVA-Ca-mont complex.
where amounts of PVA added to clay of curves 1,2, 3,4 and 5 are 0, 1.5, 5, 11, 15 %, respectively.

For the original basal spacing of Ca-Mont under this experimental condition is about 14 to 15 Å and this value is about the same with montmorillonite in which mono-layer of PVA is adsorbed in its intercrystalline lattice. But it is reasonable to consider that only the end of polymer molecules could be adsorbed on the entrance of intercrystalline surface.

The same conception may be applied to the case of Mg-Mont-PVA complex.

Some conceptions about the surface available to PVA adsorption of each clay have been obtained from the data presented in this paragraph.

Here the relationship between amount of PVA added to clay and the number of layers of PVA molecules adsorbed onto intercrystalline surface of montmorillonite with various exchangeable cations are tabulated in Table 3.3.

Table 3.3 Number of PVA molecular layers formed intercrystalline surface of montmorillonite with various exchangeable cations.

Mont	ratio of PVA added to clay			
	5	10	15	50 %
Na-Mont	P (1) p(0)	P(1)(2)	P (2)	P (4)
K-Mont	P (0) p'(1)(2)(3)	P'(2) p'(1)(3)	P'(2)(3)	P (?)
Mg-Mont	P (0) p(1)?	P (0) p(1)?	P (0) p'(1)(2)(3)	P (0) p'(1)(2)(3)
Ca-Mont	P (0) p(1)?	P (0) p(1)?	P (0) p'(?)	P (0) p'(?)

where the capital letter shows the principal parts of the complex and small letter shows the minor parts of the complex, figure shows the number of molecular layers of polymer adsorbed on inner surface of montmorillonite, letter with prime shows the low degree of orientation of adsorbed polymer molecules.

It is necessary to examine the relation between surface area available to polymer adsorption and the point of maximum flocculation of the system.

Table 3.4 shows those relationships of Na-Bent, Ca-Bent, Na-Mont and Ca-Mont.

Table 3.4 Relation between the maximum flocculation and coverage of surface of montmorillonite.

	Na-Bent	Ca-Bent	Na-Mont	Ca-Mont
surface area available	410 _m ²	70 _m ²	610 _m ²	84 _m ²
ratio of surface covered with PVA at max. flocculation	35.5 %	39.0 %	47.7 %	65.0 %

Table 3.4 shows when 35 to 40 % of the surface area available to polymer adsorption is covered with PVA molecules, Bent-PVA-water system is flocculated mostly. Here surface area available to PVA adsorption are assumed to be the total surface of Na-Bent and Na-Mont and only the outer surface of Ca-Bent and Ca-Mont. Another assumption is that at the point of the maximum flocculation of system is occurred all polymer molecules added would be adsorbed onto clay surface in the form of mono-molecular layer.

On the other hand, 48 to 65 % of surface area available to polymer adsorption must be covered with PVA molecules to make the system

of PVA-Mont maximum flocculative. In the latter case the ratio of surface area covered with PVA to the total surface area of Na-Mont is less than that of Ca-Mont. This fact shows the existence of considerable uncertainty concerning the surface area available to polymer adsorption about Ca-Mont. It was assumed that only the outer surface of Ca-Mont might be available to polymer adsorption. As discussed above, adsorption of polymer molecules might be occurred on inner surface of montmorillonite, so it is reasonable to consider that the Mont-PVA-water system shows the maximum flocculation when about a half of the surface is covered with PVA molecules, the similar consideration will be applied to the case of PVA-Bent-water system. The difference between the amount of PVA added at the maximum flocculation of Bent- and Mont-systems may be attributed to the particle size of original clay, namely the smaller the particle size, the more polymer is necessary to form particle which settle in a definite time interval.

v. Effects of salt addition

As mentioned before the mechanisms of flocculation of clay suspension by PVA are different from those by inorganic salt. In former mechanisms the formation of interparticle bridge of polymer plays an important role, while the change in zeta potential of hydrated layer of clay particle has an important meaning in the latter mechanisms. The problems among salt flocculation, flocculation with polymer molecules and the formation of PVA-montmorillonite interlamellar complex in salt solution will be discussed in this paragraph.

The reaction between clay and polymer molecules in salt solution has a practical meaning, for polymer used as soil conditioner may be supposed to react with clay particles in soil-solution and this soil solution has high salt concentration.

Clay samples used in this experiment were Na-Mont and Ca-Mont. PVA used was PVA-3 and the inorganic salts used were NaCl , CaCl_2 , AlCl_3 and sodium hexameta phosphate (NaPO_3)₆.

These inorganic salts were added to the clay suspension before 24 hours of the addition of polymer solution. Other procedures of the experiment were the same used before, The concentration of clay suspension was 0.1 %.

v-1 Effects of NaCl

In Figure 3.15 are shown the relationships of the relative turbidity vs. amount of PVA added to clay for the systems in various NaCl concentrations.

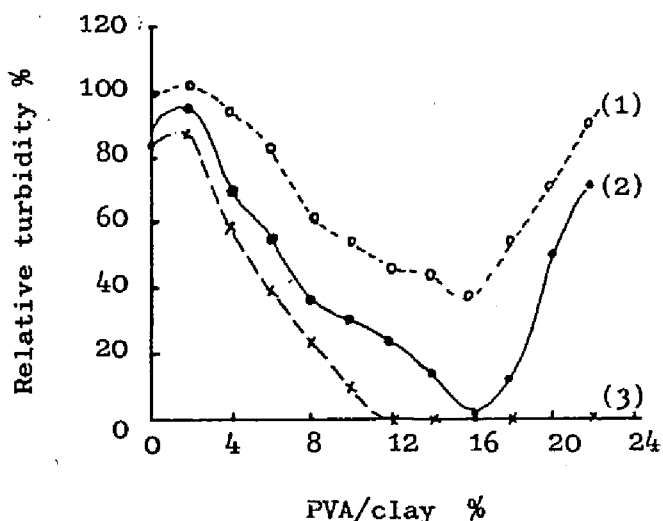


Figure 3.15 Effects of NaCl addition

where concentrations of NaCl of each system giving curves 1, 2, and 3 are 10^{-4} , 10^{-3} and 10^{-2} N, respectively.

Figure 3.15 shows that when the ratio of PVA added to clay was 16 % systems 1 and 2 show a maximum flocculation and also system 3 has the same tendency. It is inferred from these facts that the surface area of montmorillonite available to polymer adsorption would not be changed in the NaCl solution of these concentration.

X-ray analyses of those complexes were conducted so as to examine

above inference. The obtained X-ray diffraction diagrams are illustrated in Figures 3.16. and 3.17.

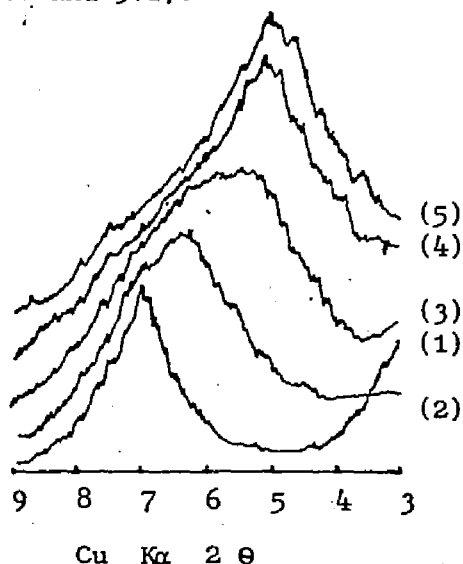


Figure 3.16 X-ray diffraction patterns of PVA-Mont complex formed in NaCl solution of 10^{-3} N. where amounts of PVA added to clay of curves 1,2,3,4 and 5 are 0, 5, 10, 15 and 20 %, respectively,

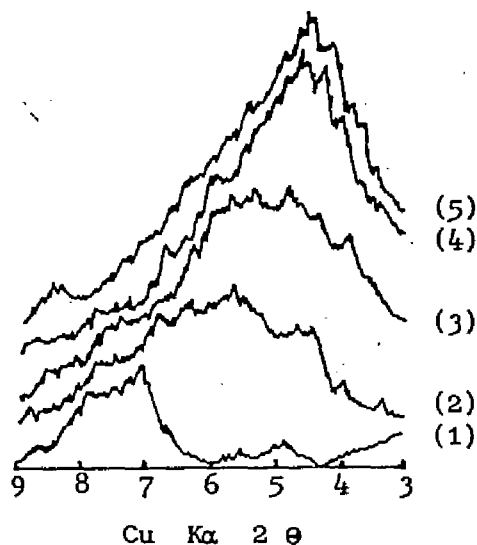


Figure 3.17 X-ray diffraction patterns of PVA-Mont complex formed in 10^{-1} N NaCl solution. where amounts of PVA added to clay of curves 1,2,3,4 and 5 are 0, 5, 10, 15 and 20 %, respectively.

Figure 3.16 shows that in this salt concentration no effect on the adsorption of PVA molecules onto intercrystalline surface of montmorillonite is observed, while diagrams in Figure 3.17 suggest that PVA molecules are adsorbed onto inner surface of montmorillonite independently from salt flocculation of clay particles, but effects on the orientation of polymer molecules adsorbed onto inner surface of montmorillonite are observed. The analogous phenomena were observed in the effects of pH of the medium on the formation of PVA-Mont interlamellar complex.

v-2 Effects of CaCl_2

In the case of CaCl_2 , the complete salt flocculation on the system was observed when the concentration of CaCl_2 was 10^{-2} N. Relationship between the relative turbidity and the amount of polymer added to clay are given in Figure 3.18.

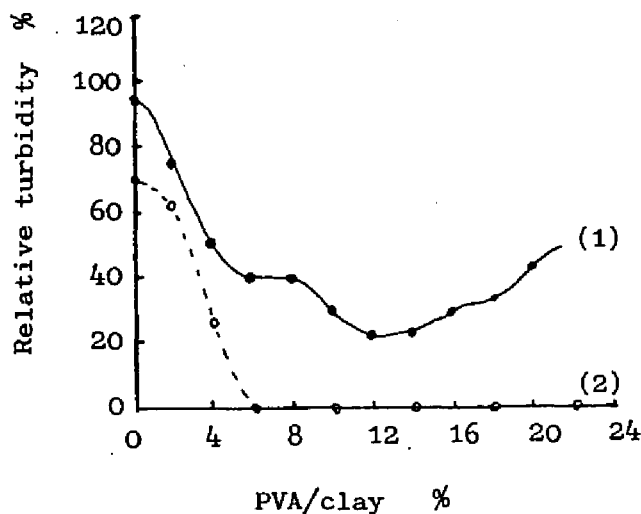


Figure 3.18 Effects of CaCl_2 on the flocculation of clay suspension with PVA.
where concentrations of CaCl_2 of curves 1 and 2 are 10^{-4} and 10^{-3} N, respectively.

Comparing curves in Figure 3.18 with those in Figure 3.15, one remarkable difference between them is observed, namely the amount of polymer added to clay in the region of optimum flocculation is 12 to 14 % in Figure 3.18, while that value in Figure 3.15 is 16 % . This difference in results of two Figures is supposed to be attributed to the change in the surface area available to polymer adsorption. This will be discussed from results of X-ray analyses for complexes.

X-ray diffraction patterns of PVA-Mont complexes formed in various concentration of CaCl_2 solutions are presented in Figures 3.19, 3.20, 3.21 and 3.22.

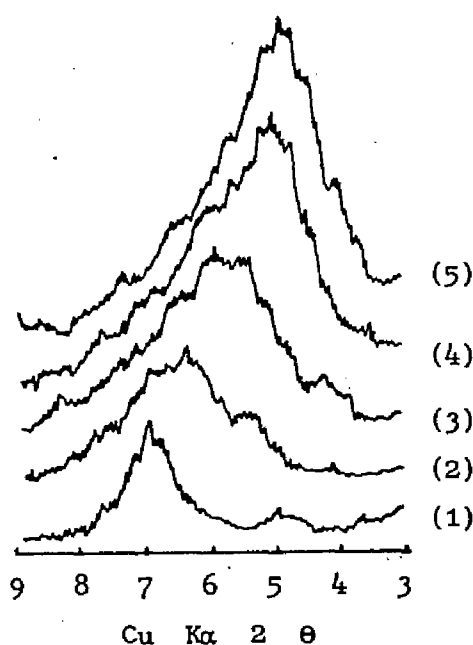


Figure 3.19 X-ray diffraction patterns of PVA-Mont complex formed in 10^{-4} N CaCl_2 solution. where amounts of PVA added to clay of curves 1,2,3,4 and 5 are 0, 5, 10, 15 and 20 %, respectively.

In these curves no remarkable changes in the formation of inter-crystalline complex are observed, and the analogous results are obtained from curves in Figure 3.20. But comparing curve 1 of Figures 3.19 and 3.20, one may notice the formation of some amounts

of calcium-montmorillonite may be formed, especially in the latter curve.

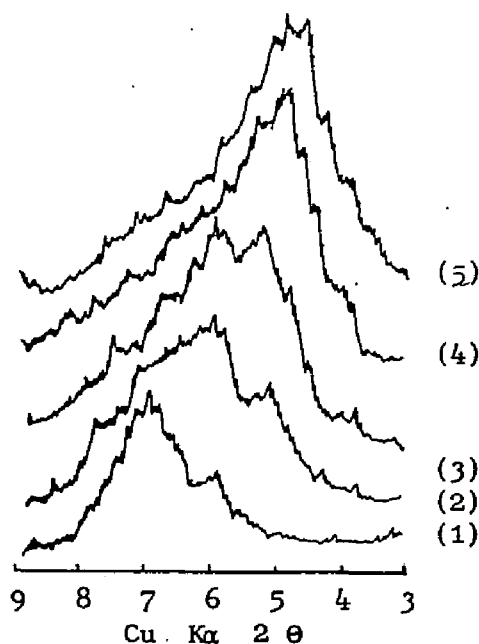


Figure 3.20 X-ray diffraction patterns of PVA-Mont complex in 10^{-3} N CaCl_2 solution: where amounts of PVA added to clay of curves 1,2,3,4 and 5 are 0, 5, 10, 15, and 20 %, respectively.

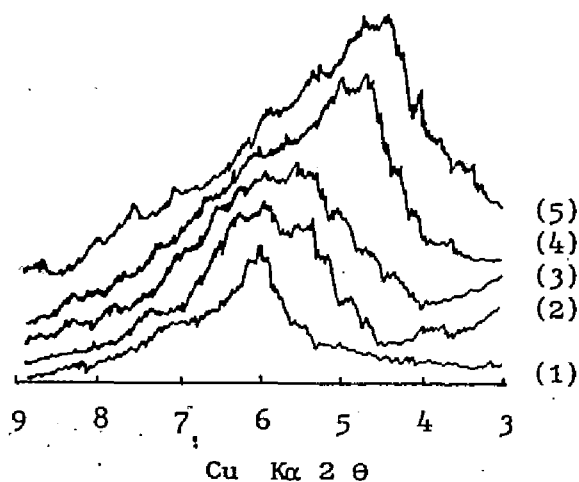


Figure 3.21 X-ray diffraction patterns of PVA-Mont complex formed in 10^{-2} N CaCl_2 solution.

where amounts of PVA added to clay of complexes giving curves 1, 2, 3, 4 and 5 are 0, 5, 10, 15 and 20 %, respectively.

This fact supports the decrease in surface area available to polymer adsorption, which causes the difference between the flocculation-de-flocculation phenomena between systems in Figures 3.17 and 3.18.

Curve 1 in Figure 3.21 and curve 1 in Figure 3.22 show that the exchangeable cation of the clay was exchanged from sodium ion to calcium ion. But curves in these two Figures show that more than two molecular layers of PVA are adsorbed onto inner surface of montmorillonite. In those cases, i.e. when multi molecular layers of PVA are formed, the basal spacing of montmorillonite must be large enough to accommodate the polymer molecule with large size, say more than 300 Å. But it has been reported that the maximum basal spacing could not accommodate the large molecule such as polyvinyl alcohol.

Here, the author found the fact that distance of (001) spacing of some calcium-montmorillonite can be more than 300 Å. This fact will be discussed later in paragraph v-4 in this chapter.

Relations between the distance of (001) spacing of montmorillonite and the concentration of salt solution in which the complex was formed are summarized in Table 3.5.

Table 3.5 The basal spacing of montmorillonite treated with PVA in CaCl_2 solution.

CaCl_2 (N)	10^{-3}	10^{-2}	10^{-1}	1
d (001) of montmorillonite (Å)	18.8	19.6	22.9	15.9
	18.4	18.5	14.7	15.0

where amount of PVA added to clay is 15 % in every samples.

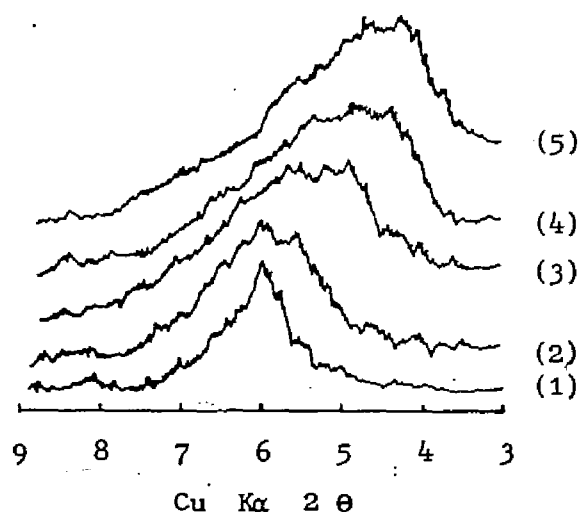


Figure 3.22 X-ray diffraction patterns of PVA-Mont complex formed in 10^{-1} N CaCl_2 solution. where amounts of PVA added to clay of patterns 1,2, 3,4 and 5 are 0, 5, 10, 15 and 20 %, respectively

Table 3.5 shows that the higher the concentration of CaCl_2 , the lower the degree of orientation of PVA molecules adsorbed onto inter-crystalline surface of montmorillonite becomes, except when the concentration of CaCl_2 is 1 N. These phenomena suggest the effects of CaCl_2 on the formation of PVA-Mont interlamellar complex. When the concentration of CaCl_2 is 1 N, PVA molecules do not be adsorbed onto inner surface of montmorillonite as multi-layers, which suggests the second flocculation of montmorillonite with salt might be occurred

v-3 Effects of AlCl_3

The turbidity measurement of system of PVA-Mont- AlCl_3 solution could not be conducted over wide AlCl_3 concentration, for the system was completely flocculated when the concentration of AlCl_3 was 10^{-3} N.

Figure 3.23 shows a relationship among relative turbidity, concentration of AlCl_3 and amount of PVA added to clay.

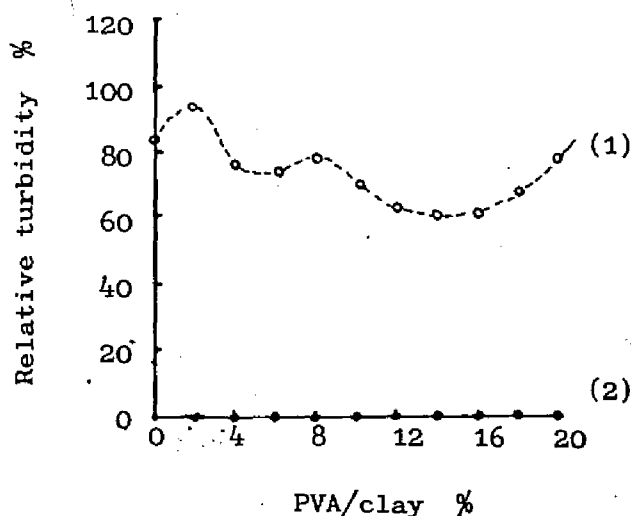


Figure 3.23 Effects of AlCl_3 on the flocculation of PVA-Mont system.

where the concentrations of AlCl_3 of systems giving curves 1 and 2 are 10^{-4} and 10^{-3} N, respectively.

Curve 1 in Figure 3.23 has two flocculating regions over the range of polymer addition of 12 to 16 %, and the mode of this curve is somewhat similar to that of curve 2 in Figure 3.10.

Considering about the form of AlCl_3 which is decided by pH of the system, pH of this system was 7.00, so the AlCl_3 added is hydrolyzed and aluminium ion produced takes the form of $\text{Al}(\text{OH})_3$, this hydroxyl aluminium would be adsorbed onto clay surface and restrict the reaction of polymer molecules and clay surface, if those $\text{Al}(\text{OH})_3$ are adsorbed onto intercrystalline surface of montmorillonite, the expansion of intercrystalline lattice of montmorillonite would be restricted to some extent. This consideration will be examined

with the results of x-ray diffraction experiments of the PVA-Mont complex formed in AlCl_3 solution.

In Figures 3.24, 3.25 and 3.26 are illustrated the X-ray diffraction patterns of PVA-Mont complexes.

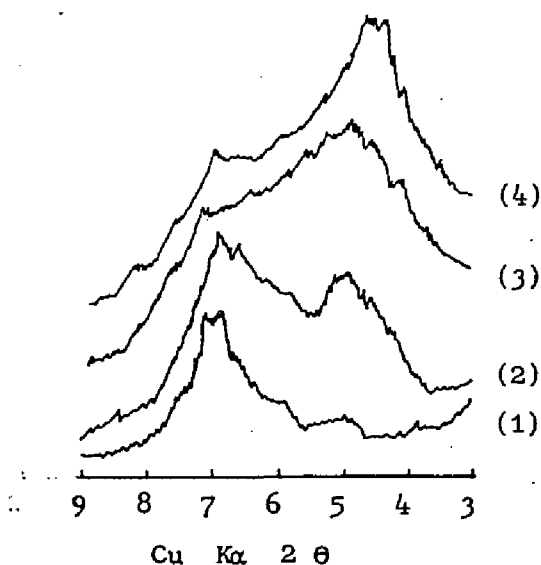


Figure 3.24 X-ray diffraction patterns of complex formed in 10^{-4} N AlCl_3 solution where amounts of PVA added to clay of curves 1, 2, 3 and 4 are 0, 8, 10 and 20 %, respectively.

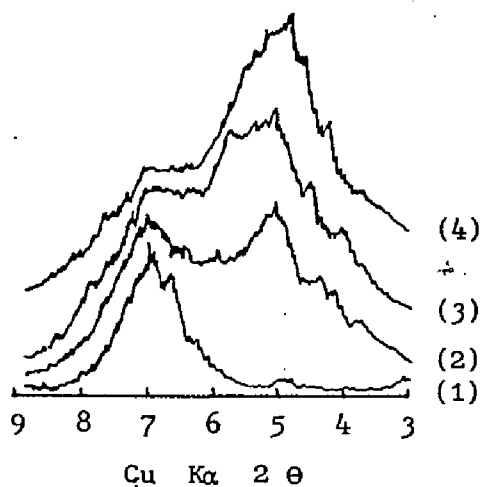


Figure 3.25 X-ray diffraction patterns of PVA-Mont complex formed in 10^{-3} N AlCl_3 solution.

where amounts of PVA added to clay of curves 1, 2, 3 and 4 are 0, 8, 10, and 20 %, respectively.

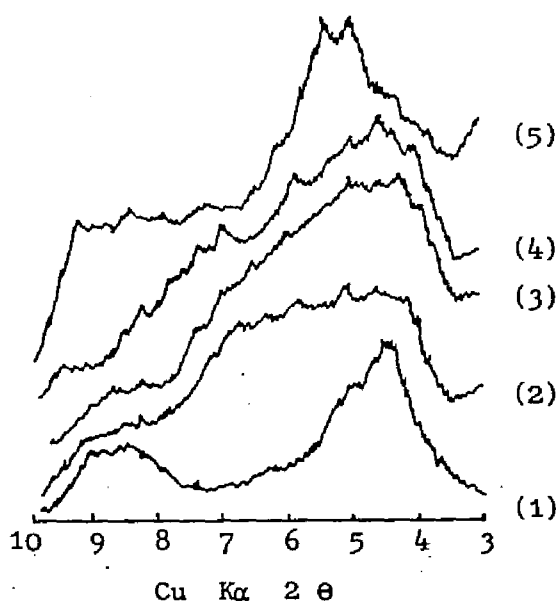


Figure 3.26 X-ray diffraction patterns of PVA-Mont complex formed in 10^{-2} N AlCl_3 solution where amounts of PVA added to clay of curves 1, 2, 3, 4 and 5 are 0, 5, 10, 15 and 50 %, respectively.

Curves 2, 3 and 4 in Figure 3.24 suggest the existence of two large constituting groups in the clay, namely one group does not absorb polymer molecules onto its inner surface and shows the diffraction peak at 7° , while the other one can absorb polymer molecules onto inner surface of montmorillonite and shows the diffraction peak in the region of lower than 5° . The analogous tendency is observed more remarkably in curves presented in Figure 3.25.

When the concentration of AlCl_3 was 10^{-3} N, pH of the system was 4.8 and under this pH value $\text{Al}(\text{OH})_3$ would not be dissolved, so the effects of aluminium hydroxyde on the formation of PVA-Mont inter-lamellar complex is inferred to be increased. In Figure 3.25, these diffraction diagrams show that the kinetic unit of montmorillonite in water suspension would be particles in which infinite numbers of

montmorillonite unit layers are involved. If the kinetic units were unit layers of montmorillonite, the X-ray diffraction diagrams of the complex would take the form of interstratified crystalline. Curves in Figure 3.26 show that large changes in the basal spacing of montmorillonite treated by PVA do not be observed with increasing of the amount of PVA addition.

pH of this system was 3.7, and under this pH value AlCl_3 takes the form of aluminium cation and chlor anion, and this trivalent cation with hydrated form occupied the exchangeable sites of clay surface, consequently large distance of (001) spacing of curve 1 in Figure 3.26 seems to be attributed to hydrated aluminium ion. So after drying at 100 °C for 24 hours, X-ray analyses of the complex were carried out.

The results of X-ray analyses are illustrated in Figure 3.27.

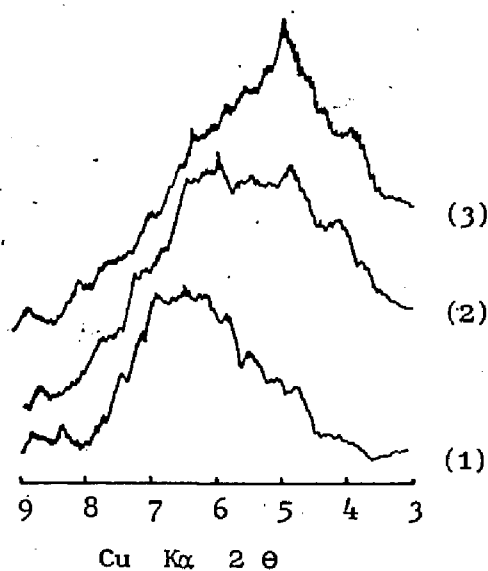


Figure 3.27 X-ray diffraction patterns of the complex after drying at 100 °C. where ratios of PVA added to clay of the complex giving patterns 1, 2 and 3 are 0, 10 and 15 %, respectively.

Curve 1 in Figure 3.27 suggests that the most of water molecules hydrated to aluminium cation would be dehydrated through drying and other two curves show that peak at 5 ° are remained unchanged through the drying, which also suggests the formation of two layers of polymer molecules in intercrystalline lattice of montmorillonite.

These facts also support the conceptions about kinetic units of montmorillonite in water which was mentioned above.

v-4 Effects of $(\text{NaPO}_3)_6$

Relationship among relative turbidity, amount of PVA added to clay and the concentration of $(\text{NaPO}_3)_6$ are illustrated in Figure 3.28.

Salt flocculation of montmorillonite suspension was observed when the concentration of $(\text{NaPO}_3)_6$ was 10^{-1} N.

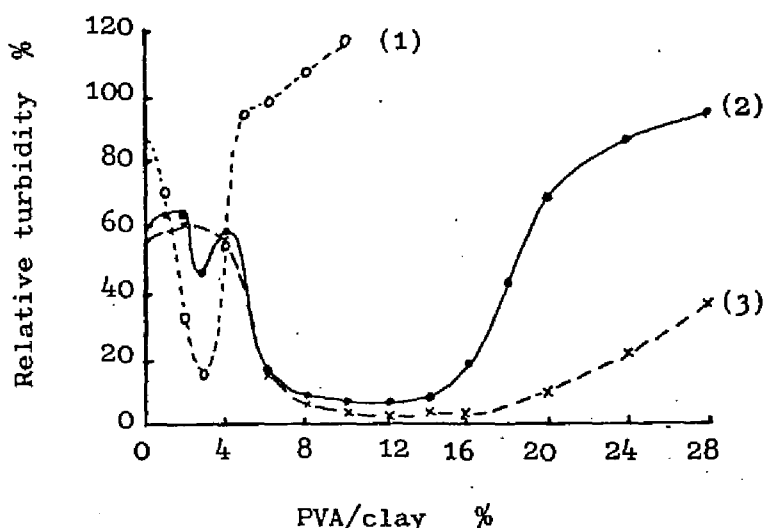


Figure 3.28 Effects of $(\text{NaPO}_3)_6$ on the flocculation of Ca-Mont-PVA system.
where the concentrations of $(\text{NaPO}_3)_6$ the systems 1, 2 and 3 are 10^{-4} , 10^{-3} and 0.01 N, respectively.

Curve 1 in Figure 3.28 has almost the same form with that of curve 4 in Figure 10, on the other hand, curve 2 in Figure 3.10

shows the resemblance in its form to curve 1 of Figure 3.23, the resemblance in its form suggests the existence of more than two constituting groups which have different intercrystalline expansive properties.

X-ray diffraction patterns of these complexes will be shown in relation to these two groups. Curve 3 in this Figure shows wide flocculating region suggesting the salt flocculation, and characteristic behaviours of PVA-Ca-Mont system could not be observed in this curve. Those data show the surface area of Ca-Mont available to the adsorption of polymer molecules was increased by treating with $(\text{NaPO}_3)_6$.

X-ray diffraction patterns for Ca-Mont treated with various concentration of $(\text{NaPO}_3)_6$ solution are illustrated in Figure 3.29

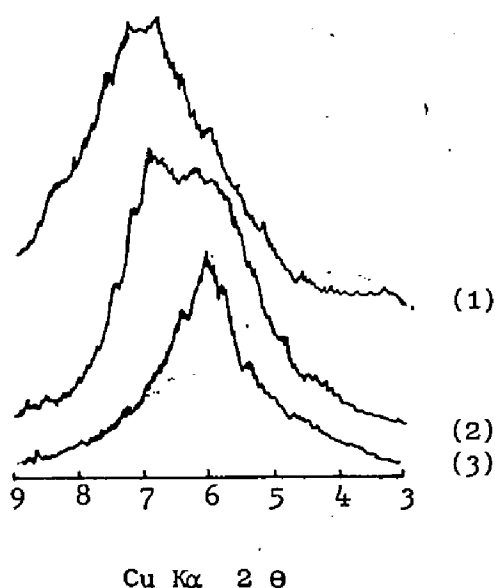


Figure 3.29 X-ray diffraction patterns of Ca-Mont treated with $(\text{NaPO}_3)_6$ where the concentrations of $(\text{NaPO}_3)_6$ of the systems 1, 2 and 3 are 10^{-4} , 10^{-3} , and 10^{-2} N, respectively.

The mode of curve 1 in Figure 3.29 is almost the same with that of curve 1 in Figure 3.14 and this fact explains the position of the maximum flocculation of suspension system, while when the concentration of $(\text{NaPO}_3)_6$ is 10^{-3} N, i.e. in curve 2, the basal spacing of clay becomes to 12.3 Å, though a shoulder of diffraction of Ca-Mont is remained at 6° . Here the existence of two groups with different expanding characters in this clay is clarified and this fact explains two maximum flocculating regions of curve 2 in Figure 3.28. Curve 3 in this Figure suggests the exchangeable cation of the clay was changed completely to sodium ion, so this clay has large surface area available to the polymer adsorption than Ca-Mont.

Change in the surface area available to polymer adsorption of Ca-Mont was also clarified through the degree of formation of PVA-Mont interlamellar complex. X-ray diffraction diagrams of the PVA-Mont complex formed in various concentration of $(\text{NaPO}_3)_6$ solution are presented in Figure 3.30.

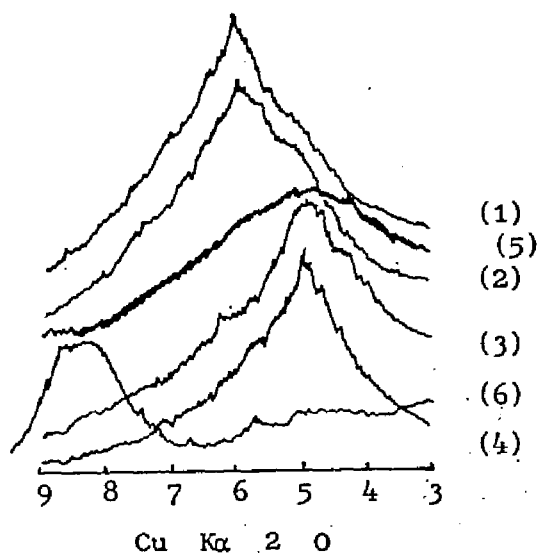


Figure 3.30 X-ray diffraction patterns for PVA-Mont complex formed in $(\text{NaPO}_3)_6$ solution.

where the concentrations of $(\text{NaPO}_3)_6$ of curves 1, 2, 3, 4, 5 and 6 are 0, 10^{-4} , 10^{-3} , 10^{-2} , 1 and 2 N, respectively

amount of PVA added to the system was 16 % .

Figure 3.30 shows that complete interlamellar complex of PVA-Mont is formed over the region of $(\text{NaPO}_3)_6$ concentraion of 10^{-3} to 10^{-1} N, and the formation of interlamellar complex can not be observed when the concentration of $(\text{NaPO}_3)_6$ is 2 N, but when it is 10^{-4} and 1 N, partial formation of the complex is observed.

The phenomena of flocculation-deflocculation of the system of PVA-Ca-Mont- $(\text{NaPO}_3)_6$ solution are completely explained by the data shown in Figure 3.30.

vi. Behaviours of calcium-montmorillonite in water

It has been said that the basal spscing of calcium-montmorillonite in water is almost 20 Å and the further expansions of intercrystalline lattice do not be observed in calcium-montmorillonite. But the author observed the existance of calcium-montmorillonite with more expansible properties in the former paragraph.

In order to certify these behaviours of calcium-montmorillonite in water suspension, the flocculation and deflocculation of montmorillonite suspension as affected with PVA will be studied in this paragraph.

Besides flocculation-deflocculation experiments, technique of X-ray diffraction analysis was also employed.

The kinetic unit of montmorillonite in water suspension will be also studied in this paragraph.

Flocculation and deflocculation behaviours of montmorillonite suspension.

Three series of montmorillonite samples were offered to this experiment. Ca-Mont was prepared from Na-Mont suspension by washing with CaCl_2 solution. After exchanging all sodium ions for calcium ions, one part of calcium-montmorillonite suspension was dried at 50 °C, then this dried clay was again dispersed in water to get clay suspension, this sample was designated as Ca-Mont-dried, another part of exchanged suspension was used without any treatment.

This clay sample was designated as Ca-Mont-undried.

Organic polymers used were PVA-1, PVA -3 and PVA-4.

Figure 3.31 shows the relations among the difference of clay, amount of PVA added to clay and relative turbidity of the system.

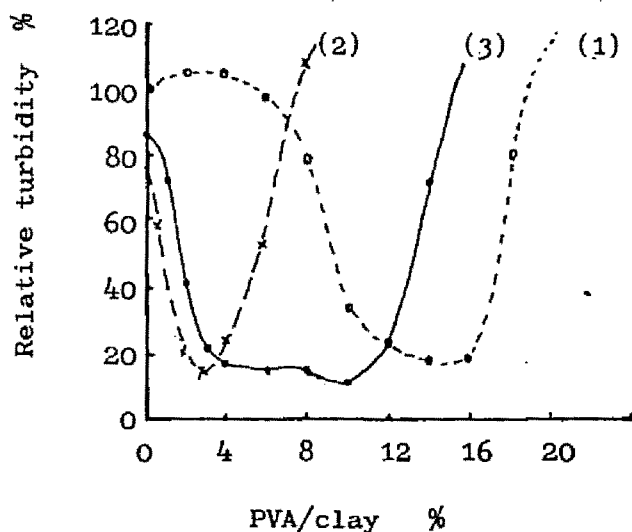


Figure 3.31 Results of flocculation -deflocculation experiment where clay of the systems giving curves 1, 2 and 3 are Na-Mont, Ca-Mont-dried and Ca-Mont-undried, respectively.

Figure 3.31 shows that amounts of PVA added to clay at the maximum flocculating point of these systems are different from each other and amounts of polymer added at those points are tabulated in Table 3.6.

Table 3.6 Relations between the maximum flocculating point and the amount of PVA added at the point.

	Ca-Mont dried	Ca-Mont undried	Na-Mont
% of PVA at max. floc.	3.4	9	16

The most remarkable facts deduced from this Table is that the surface area available to the adsorption of polymer molecules of Ca-Mont-undried is larger than that of Ca-Mont-dried and smaller than that of Na-Mont.

It is reasonable to suppose that the difference between the surface area of Ca-Mont dried and that of Ca-Mont undried would be attributed to difference of intercrystalline surface available to adsorption of PVA molecule. On the other hand, as mentioned before, the system of Mont-PVA-water shows the maximum flocculation when a certain ratio of the total surface area is covered with PVA mono-molecular layer, and this ratio was given in Table 3.4. From those ratios the surface area of Ca-Mont-undried available to PVA adsorption will be calculated. Now 48 % is taken up as this ratio, the surface area is calculated as follow;

$$x \cdot \frac{48}{100} = 1820 \cdot \frac{9}{100} \quad \text{so} \quad x = \frac{1820 \cdot 0.09 \cdot 100}{48}$$

where x is the surface area of Ca-Mont-undried in squer meters per one gram of clay, 1820 is the area of one gram of PVA in mono-layer state (squer meters), 0.09 is weight of PVA added to one gram of Na-Mont when the maximum flocculation was occured (gram).

Here the surface area of Ca-Mont-undried was calculated as 340 m^2 per one gram of clay.

And it was also calculated that 49 % of Ca-Mont-undried have large basal spacing, say more than 300 Å.

From those data, it is decided that non-expansible character of Ca-Mont is brought about completely through drying process.

X-ray diffraction analyses of the PVA-Mont complexes.

X-ray diffraction diagrams for the Ca-Mont-dried-, Ca-Mont-undried- and Na-Mont-PVA complexes are illustrated in Figure 3.32.

Curve 1 in Figure 3.32 suggests that PVA molecules do not be adsorbed on inner surface of Ca-Mont-dried as two molecular layers,

while curve 3 shows that all montmorillonite absorbs two molecular layers of PVA in its intercrystalline surface.

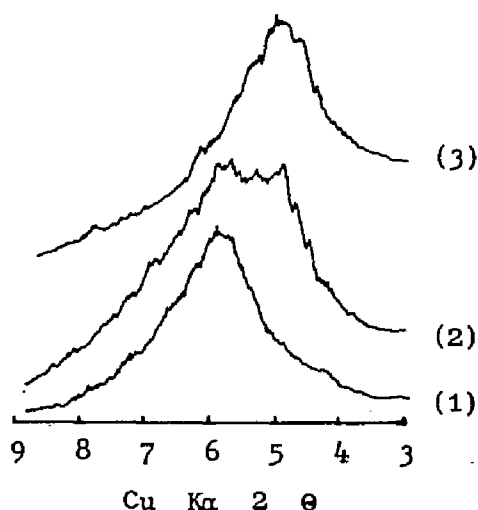


Figure 3.32 X-ray diffraction patterns of PVA-Mont complexes where clay of sample giving diffraction patterns 1,2 and 3 are Ca-Mont-dried, Ca-Mont-undried and Na-Mont, respectively. amount of PVA added to clay was 20 % in every sample.

It is considered from the curve 2 that PVA-Ca-Mont-undried consists of two type of complexes, one is PVA-Ca-Mont-dried type and the other is PVA-Na-Mont type complex. Here it is clarified that the existence of Ca-Mont with large basal spacing in water.

In order to know the amount of expansible and non-expansible particles in Ca-Mont-undried, it was tried to measure the area of X-ray diffraction peaks of complexes.

Firstly the measurement was done about the mixture samples of PVA-Ca-Mont-dried and PVA-Na-Mont complexes.

X-ray diffraction diagrams of these samples are illustrated in Figure 3.33.

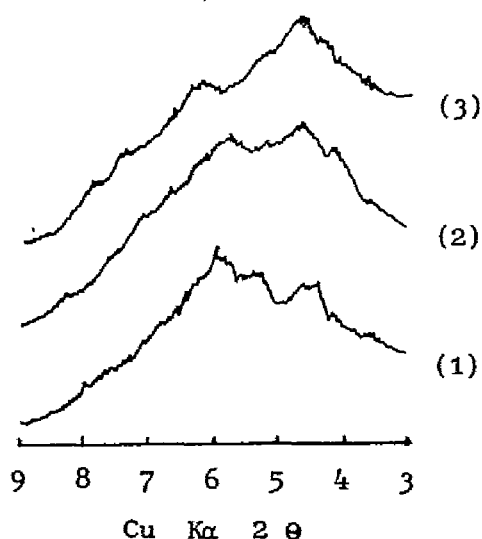


Figure 3.33 X-ray diffraction patterns of mixture of two type of complexes.
where ratios of Ca-Mont-dried-PVA : Na-Mont-PVA complex of diffraction patterns 1,2 and 3 are 60 : 40, 50 : 50, 40 : 60, respectively.

Each peak is composed from two peaks ,i.e. one is the peak due to the PVA-Ca-Mont-dried complex and the other is due to the complex of PVA-Na-Mont, so these peaks may be divided into original two peaks as shown in Figure 3.34.

Relationships between peak area measured and the ratio of the weight of two complexes mixed are given in Table 3.7.

Table 3.7 shows that the peak area is nearly equivalent to the ratio of weight of complexes mixed. This fact suggests that one can measure the different constituting elements in Ca-Mont-undried from the measurement of the peak area of its X-ray diffraction diagram.

The divided form of the diffraction peaks of Figure 3.32 are represented in Figure 3.35.

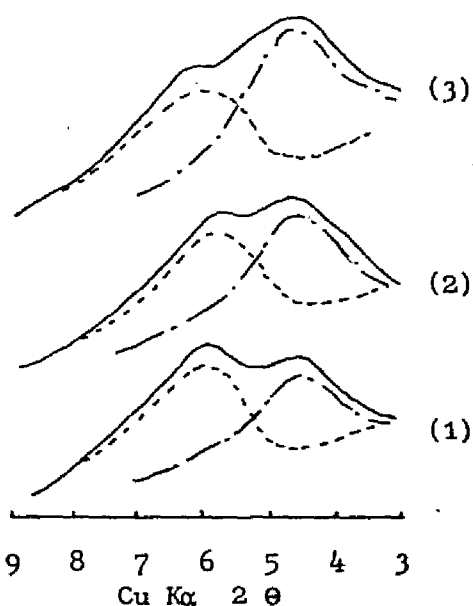


Figure 3.34 X-ray diffraction diagrams divided into constituting elements.
where dotted line shows the complex of Ca-Mont-dried-PVA and dashed line presents the complex of PVA-Na-Mont.

Table 3.7 Peak area of diffraction diagrams of complexes mixed.

	Ca-Mont : Na-Mont		
Mixing ratio	60 : 40	50 : 50	40 : 60
Ratio of peak area	58 : 42	51 : 49	40 : 60

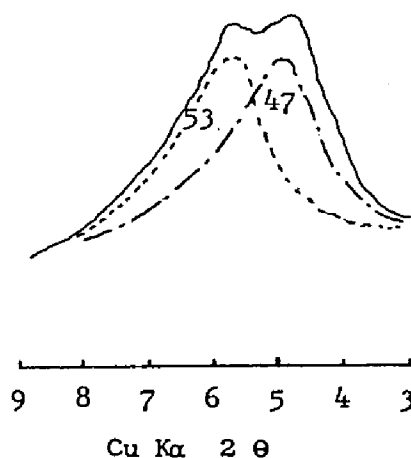


Figure 3.35 Separation of X-ray diffraction peak into original two diffraction peaks. where the dotted line is due to the PVA-Ca-Mont-dried complex and dashed line presents the peak due to PVA-Na-Mont complex.

The area of these two peaks was measured to be a ratio of 4.7 : 5.3 . And it was calculated that 47 % of Ca-Mont-undried is expansible enough to accomodate large PVA molecules in its inter-crystalline surface.

If one uses the different size of polymer molecules to make interlamellar complex with Ca-Mont-undried, more detail separation of particles with different expansibility will be able to do.

The author divided Ca-Mont-undried to more detail parts by using PVA-1, PVA-3 and PVA-4.

Combining the results of peak analyses and the molecular size presented by Hosono et al⁴⁹⁾, Ca-Mont-undried was separated according to its expansibility.

CHAPTER 4

WATER STABILITY OF DRY POLYVINYL ALCOHOL-MONTMORILLONITE COMPLEXES

The phenomena of flocculation-deflocculation of clay suspension as affected by the addition of PVA suggest the reaction between PVA molecules and clay particles. But characters of PVA-Mont complex formed in suspension are inferred to be changed through drying. Here in this chapter, one of character of the dried PVA-Mont complex will be discussed

Water stability of the dried complex is taken up as this character for this character seems to have an intimate relation with the existing state of polymer molecules in the complex and this may give some answers about the problems of the changes in the state of adsorbed polymer molecules, which were brought about through drying process.

Moreover water stability of the complex has an practical meaning, for the basic materials of the soil conditioner devised by Kita et al⁵⁸⁾ are supposed to be the reaction products of PVA and Bentonite.

On the other hand, it is supposed that this PVA-Mont complex would play an important role in the ion exchange material made from PVA and Bentonite⁵⁹⁾.

It is necessary for this complex to have water stable characters.

From this point, it also becomes necessary to study the water stable characters of dried PVA-Bent complex.

Without passing through drying process, PVA-Bent complex has no water stable character.

Some factors which are supposed to have effects on the water stability of dried complex will be treated in following paragraphs.

4.1 Materials and methods

Clay samples used in this experiment were Na-Bent and Ca-Bent

and organic polymer used was PVA-3.

Method

Preparation of the dried complex

Increasing amount of PVA solution was added to definite amount of clay suspension, after mixing the system by a home mixer for five minutes, the system was stood for 24 hours at room temperature. At the end of this time interval, this system was put into the vessel of high vacume and the air trapped in the system was suctioned out, then the complex gained was dried at 50 °C. The dried complex was crushed into crumbs of 2-4 mm in its diameter, and these crumbs were offered to water stability test. On the other hand, a part of dried complex was crushed to finer particles and offered to X-ray diffraction analysis.

One of the process of preparation of complex crumbs is given in Scheme 4.1 and the different procedure employed will be mentioned in its place.

Measurement of water stability of dried complexes

Various methods of water stability test for soil aggregates were devised. 13), 16), 66), 105)

Here one of these methods proposed by Kawaguchi and Kita 54), 55) was employed. In this method, crumbs of 2-4 mm were seaved in water with various opening seaves, for example, 4 mm, 2 mm, 0.5 mm and 0.1 mm. The crumbs remained on each seave was dried at 50 °C and measured the weight of the dried crumbs. Each value was presented as the percentage against the weight of the original sample offered.

Crumbs larger than 2 mm are called as water stable crumbs, and the sample involving more than 90 % of water stable crumb is called as it has complete water stability.

4.2 Results and discussions

1. Effects of clay concentration

The basal spacing of sodium montmorillonite is affected by the amount of water in the system of clay-water, for example the larger

The results obtained are tabulated in Table 3.8.

Table 3.8 Separation of Ca-Mont-undried according to its expansibility.

D.P. of PVA	Effective diameter	% of complex
300	80 A	65
1700	300 A	47
2700	400 A	48

Here there is an assumption that in order to form two molecular layers of PVA in intercrystalline lattice of montmorillonite, the basal spacing of montmorillonite must be nearly equal to the size of polymer molecules in water.

It is clarified that more than 65 % of particles have the expansible character and it was also certain that the amount of this expansible part is decreased with centrifugal treatment. It shows that the gravitrical force applied on clay particles also brings some parts of them into intercrystalline flocculation.

3.3 Summary

From the experimental data obtained in this chapter, it is summarized as follow;

When increasing amount of PVA is added to clay suspension, the system shows the maximum flocculation at a certain amount of polymer added to clay, and over this amount the system begins to deflocculate again.

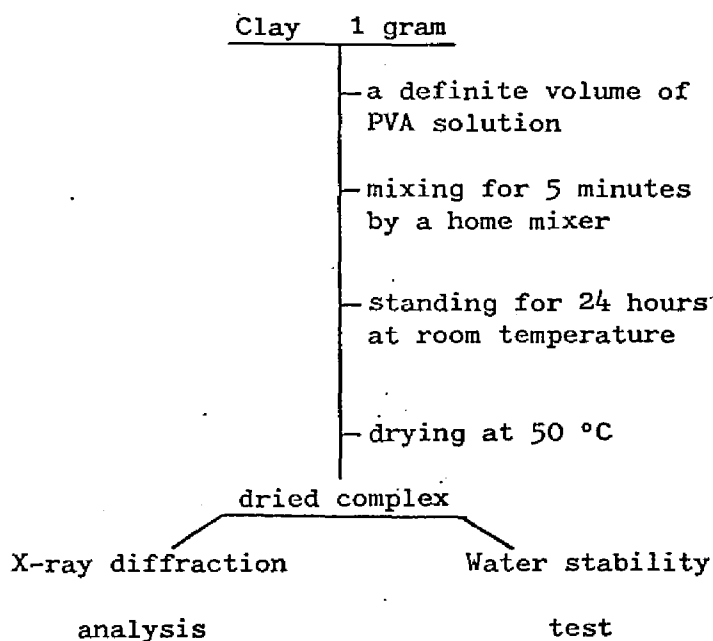
The amount of polymer added to bring the system to the maximum flocculation is affected with surface area available to polymer adsorption, and this surface area available to polymer adsorption is affected by exchangeable cations of clay, pH of medium and salt concentration of the system.

The affective sites of polymer molecules for flocculation of clay particles are intruding parts of polymer molecules adsorbed onto clay surface.

The main flocculating mechanism of polymer is the formation of polymer bridge between clay particles. The higher the degree of polymerization of polymer, the larger the flocculating power of polymer becomes.

The kinetic unit of montmorillonite in water is particle in which infinite number of unit layers are involved.

Calcium montmorillonite prepared from sodium montmorillonite suspension has large basal spacing before drying, and after drying it loses its expansible character.



Scheme 4.1 Preparation of complex crumbs

Table 4.1 Distribution of crumbs after water stability test.

Sample used 2- 4 mm 10 g.

PVA/Bent %	Distribution of crumbs (g.)		
	4 mm	2 - 4 mm	2 - 0.5 mm
2	—	2.10	1.90
3	0.40	3.70	2.67
4	0.35	3.85	2.44
6	0.97	5.03	2.40
8	7.02	3.58	0.40
10	8.00	1.90	0.14
12	7.35	2.25	0.10

the amount of water in the system, the larger the distance of (001) spacing of sodium montmorillonite becomes, and vis vasa. So the adsorption of PVA molecules onto intercrystalline surface of montmorillonite will be affected by the amount of water in the clay-PVA-water system.

It is also supposed that the states of polymer molecules adsorbed onto clay surface would have an intimate relation with the water stability of PVA-Mont complexes.

Relation between water stability of complex and water amount of the system during the reaction of PVA and clay will be discussed in this section. Firstly relations between water stability of complex formed under the existence of enough amount of water for the expansion of intercrystalline lattice of montmorillonite were examined.

Results of measurements of water stability of crumbs are tabulated in Table 4.1. Here the amount of the water stable crumbs seems to represent one of the water stable characters of complex.

A relationship between the amount of polymer added to clay and amount of water stable crumbs of the samples is presented in Figure 4.2.

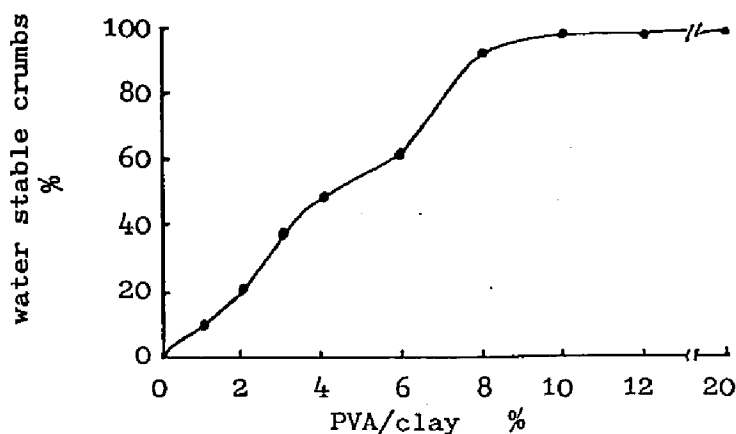


Figure 4.2 A relationship between the amount of polymer added and amount of water stable crumbs.

The most remarkable feature of Figure 4.2 is that when more than 8 % of polymer is added to clay, the formed complex has complete water stability.

Another feature of the sigmoid curve suggests a relation between two forces working in a crumb in water i.e. between force working for the breaking up of the crumb and force working against the former one. Here the former force seems to be attributed to the swelling force of clay and dispersion force of clay particles, but the dominant force is swelling one which brought about by the hydration of exchangeable cations and intercrystalline surface of montmorillonite.

The force counteracting for breaking force is brought by polymer molecules adsorbed onto clay surface. PVA molecules adsorbed onto clay surface have two roles for water stability of the complex. One is the polymer molecules adsorbed onto intercrystalline surface of montmorillonite, which change the hydration property of montmorillonite surface. Another is the polymer adsorbed onto outer surface of clay, which bonds clay particles not so as to be broken down by dispersing force.

One can see the equilibrium relations of these opposite forces are in the complex involving 5 to 6 % of PVA to clay in Figure 4.2.

Now assume that force working for the breaking up of crumb takes a constant value, so water stability of a complex will be changed by the state of adsorbed polymer molecules onto clay surface in the complex. In other words, there will be a probability of knowing the state of adsorbed polymer molecules through water stable characters of the complex. Of course X-ray diffraction analyses have an important meaning in the experiment.

In following four Tables, the results of water stability test of complex formed under conditions of polymer content of complex is constant while the water amount of the system during reaction is different from each other, are presented

In Figure 4.3 are illustrated the amount of water stable crumbs

Table 4.2 Distribution of crumbs after water stability test

Sample used 2- 4 mm 10 g. PVA/clay : 15 %

PVA solu./clay (ml/gram)	Distribution of crumbs (g.)		
	4 mm	4 - 2mm	2 - 0.5 mm
1.5	5.70	2.25	0.35
2	6.85	1.92	0.15
4	7.45	1.70	0.05
8	7.77	1.80	0.05

Table 4.3 Distribution of crumbs after water stability test

Sample used 2-4 mm 10 g. PVA/clay : 10 %

PVA solu./clay (ml/gram)	Distribution of crumbs (g.)		
	4 mm	4 - 2mm	2 - 0.5 mm
1	1.60	3.47	1.52
1.5	4.53	2.55	0.96
2	4.55	3.65	0.72
4	7.87	2.52	0.05
6	7.10	2.27	0.15
8	6.50	3.20	0.22
10	6.00	3.75	0.20

Table 4.4 Distribution of water stable crumbs

Sample used 2-4 mm 10 g. PVA/clay : 8 %

PVA solu./clay (ml/gram)	Distribution of crumbs (g.)		
	4 mm	4 - 2 mm	2 - 0.5 mm
1	0.21	2.80	2.07
2	4.14	2.90	0.81
3	3.15	5.80	0.34
4	5.10	4.30	0.10
6	4.40	5.00	0.15
8	1.70	6.65	1.20

Table 4.5 Distribution of crumbs after water stability test

Sample used 2-4 mm 10 g. PVA/clay : 6 %

PVA solu./clay (ml/gram)	Distribution of crumbs (g.)		
	4 mm	4 - 2 mm	2 - 0.5 mm
1.5	1.77	3.30	1.73
2	2.80	3.80	1.45
3	5.45	3.72	0.25
4	7.05	2.22	0.23
6	5.83	2.90	0.32
8	0.45	6.27	2.18
10	0.35	5.55	2.20

vs. the amount of water added to clay.

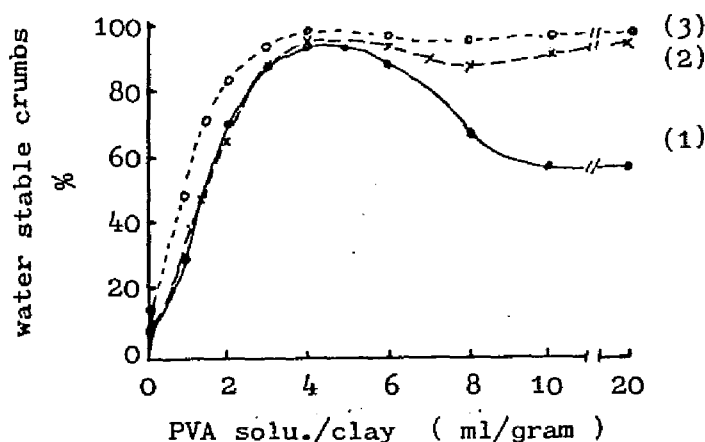


Figure 4.3 Relationship between the amount of water atable crumbs and water added to clay during reaction. where water dissolves a difinite amount of PVA and the content of polymer of complex presented curves 1, 2 and 3 are 6, 8 and 10 %, respectively.

Figure 4.3 shows that water stability of the complex is largely affected by conditions under which reaction of polymer molecules and clay particles were carried out. This effect is observed remarkably in curve 1. Analogous effects are observed in other two curves.

Here effects of polymer states in the complex are supposed to be presented as the higher water stability of the complex formed under the condition of the amount of water during reaction of polymer and clay were 3 to 6 (ml. of water / gram of clay).

It is reasonable that this effect is appeared remarkably in the series of samples given in curve 1, because as mentioned before the equilibrium relation between two opposite forces is supposed to be

in the complex of this series. So a little changes in the state of polymer molecules adsorbed onto clay surface would be appeared as the changes in water stability of the complex.

X-ray diffraction diagrams for complex shown in Figures 4.4, 4.5 and 4.6 will give some explanations about relations between water stability of complex and the state of polymer adsorbed.

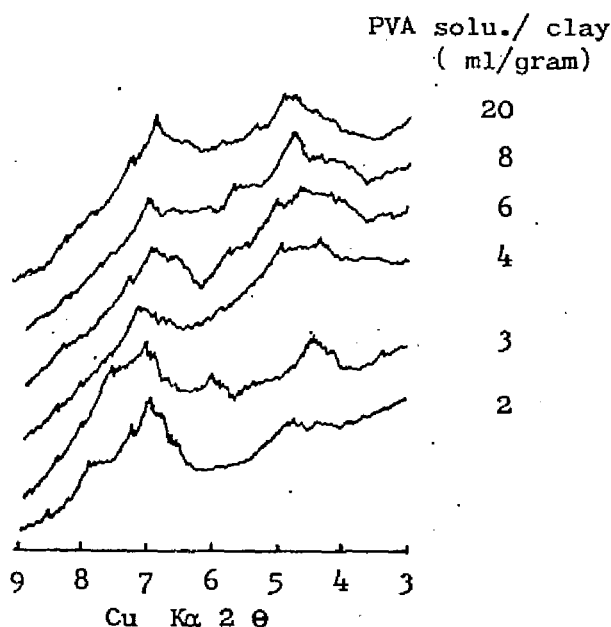


Figure 4.4 X-ray diffraction diagrams of complex involving 6 % of PVA

Figure 4.4 shows that area of diffraction peak due to montmorillonite at 7 ° decreases with the increase of water added to clay, while that of montmorillonite absorbing PVA molecules onto intercrystalline surface at 5 ° increases with the increase of water added to clay. This relation between the amount of water added to clay and the degree of formation of PVA-Mont interlamellar complex are shown more clearly in X-ray diffraction diagrams in Figures 4.5 and 4.6. X-ray diffraction diagrams in these three figures suggest that the polymer molecules adsorbed onto surface of montmorillonite play an

important role in the higher water stability shown in curve 1 in Figure 4.3.

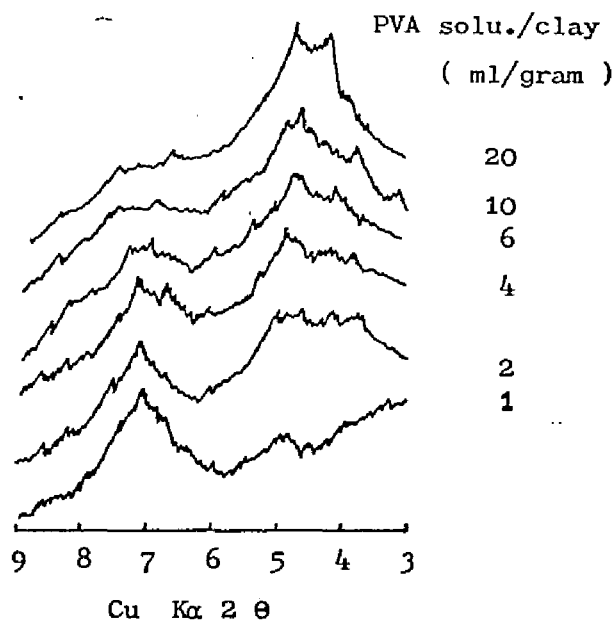


Figure 4.5 X-ray diffraction patterns of complex involving 8. % of PVA

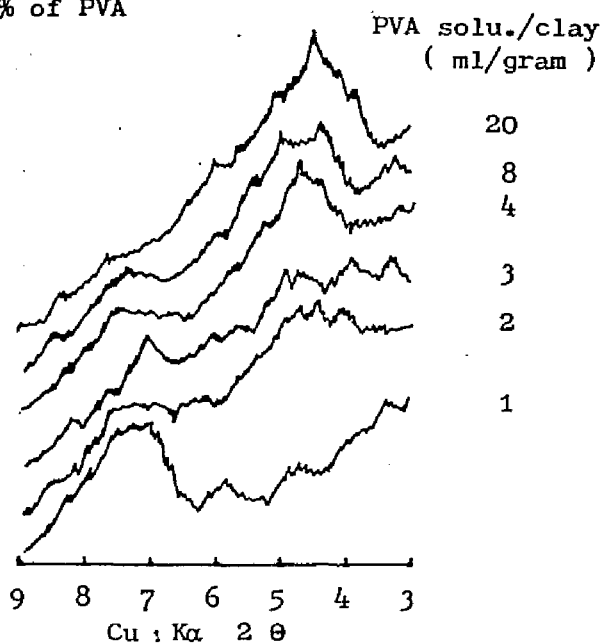


Figure 4.6 X-ray diffraction patterns of complex involving 10 % of PVA.

Polymer molecules adsorbed onto inner surface of montmorillonite restrict the hydration of inner surface of montmorillonite and so hinder intercrystalline expansion of montmorillonite. On the other hand, polymer molecules adsorbed onto outer surface of clay not only hinder the hydration of outer surface of montmorillonite but also they restrict the diffusion of water molecules into inner surface of montmorillonite, moreover they bond clay particles not so as to be broken down.

Considering from these roles of polymer molecules adsorbed onto outer surface of montmorillonite, it is inferred that water stability of complex would become higher with the increase of the amount of polymer adsorbed onto outer surface of clay.

Figure 4.7 shows the distribution of polymer molecules in a complex in relation to water amount of the system.(in the speculation)

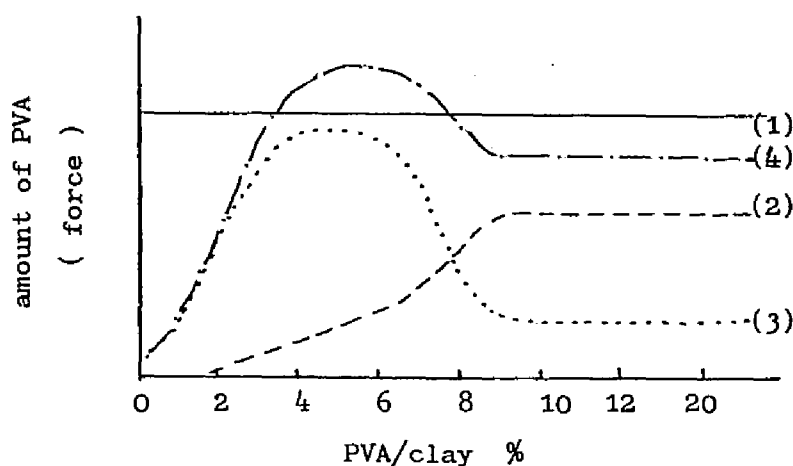


Figure 4.7 Distribution of polymer in complexes.

where curves 1, 2, 3 and 4 present: expanding force of complex, bonding force by polymer molecules

adsorbed onto inner surface that of outer surface and total bonding force of polymer adsorbed onto clay surface, respectively.

In the part of curve 4, where bonding force is larger than curve 1, the complex has about complete water stability.

These inference will be examined quantitatively in Chapter 6.

Process of adsorption of polymer molecules onto inner surface of montmorillonite

Water layers adsorbed on clay surface have some effects on adsorption of polymer molecules.

Complex used in this experiment was prepared in different procedure from that employed to make the former complexes.

Procedures of preparation of complex used in this experiment are given in Scheme 4.8.

Bent 1 gram		Bent 1 gram	
—water	a ml	PVA solu.	a ml
—	mixing by a home mixer	—	
—	standing for 24 hours	—	
—PVA solu.	8-a ml	water	8-a ml
—	mixing for a home mixer	—	
—	standing for 24 hours	—	
	at room temperature		
—	drying at 50 °C	—	
Dry complex B		Dry complex A	

Scheme 4.8 Procedures of preparation of complexes

where ratio of polymer added to clay is 10 % and amount of water added to clay is 8 ml per one gram of clay in sum. This amount of water seems to give sufficient expansion of intercrystalline lattice of clay for adsorption of polymer molecules.

A relationship between the amount of water stable crumbs and PVA added to clay is illustrated in Figure 4.9.

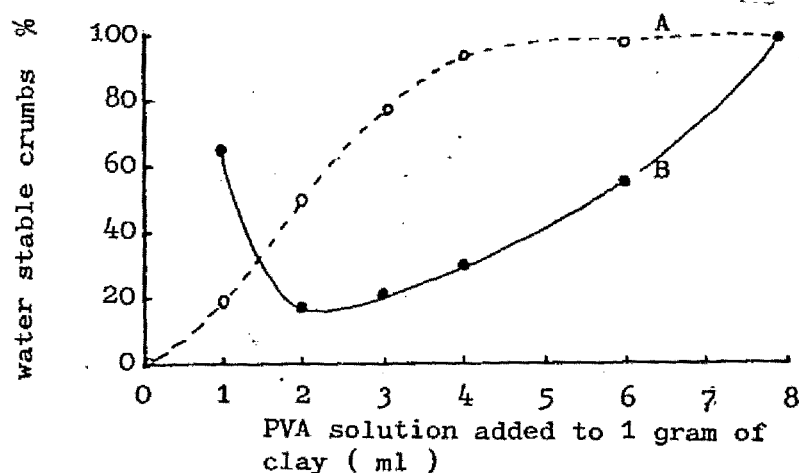


Figure 4.9 Effects of the difference of preparing process on the water stability of complexes. where curve A presents the relationship of the complex prepared by procedure A and curve B shows that by procedure B

X-ray diffraction patterns for these complexes are illustrated in Figures 4.10 and 4.11.

Diffraction patterns in Figure 4.10 show the resemblance to those in Figure 4.6, but adsorption of polymer molecules onto inner surface of montmorillonite is remarkably decreased in the complex formed by method B, which suggests that water layers formed before polymer addition would hinder the diffusion of polymer molecules into inter-crystalline lattice of montmorillonite, for those X-ray diffraction diagrams show that the adsorption of polymer molecules onto inner surface of montmorillonite could not be observed so much as in the complex prepared by method A.

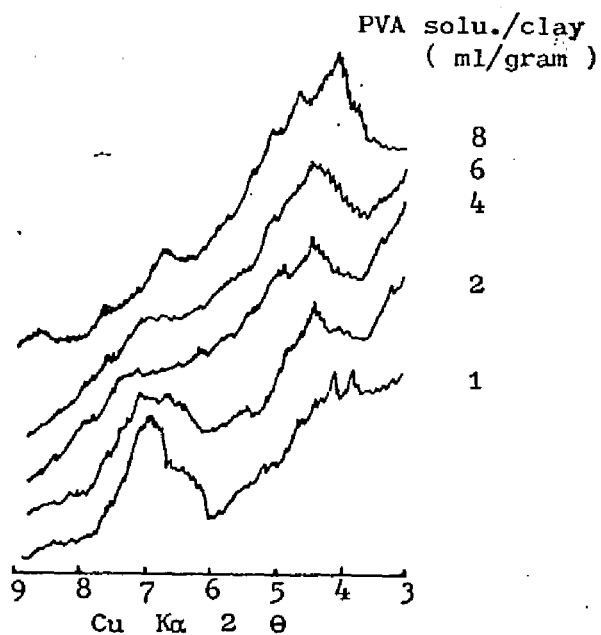


Figure 4.10 X-ray diffraction patterns for the complex A

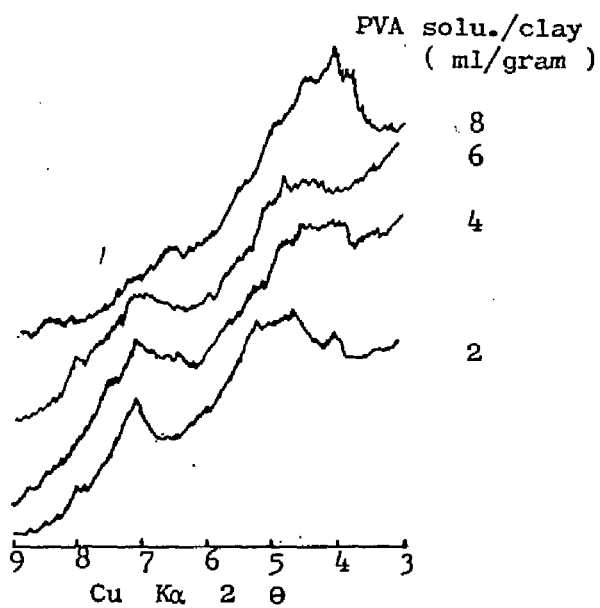


Figure 4.11 X-ray diffraction patterns for the complex B

These results suggest that expanding force of montmorillonite and the diffusion force of polymer molecules are in connection with adsorption of polymer molecules onto inner surface of montmorillonite.

ii. Effects of pH in the medium

Effects of pH of the medium on flocculation-deflocculation phenomena of PVA-Mont-water system were discussed in the former Chapter, and it was clarified that adsorption of PVA molecules onto inner surface of montmorillonite is restricted by the concentration of hydrogen ion in the system.

It will be discussed that water stability of the complex formed under different pH of the system in this section.

Reaction of montmorillonite and PVA was carried out under the condition of enough amount of water for expansion of intercrystalline lattice of montmorillonite and pH of the system was adjusted with HCl.

In Table 4.6 is tabulated the distribution of crumbs after the water stability test of the complexes.

Table 4.6 Distribution of water stable crumbs after water stability test. Sample used 2-4 mm 10 g.

pH	Amount of water stable crumb (g.)				
	7.00	6.30	4.60	3.90	2.15
PVA/clay					
1	0.07	0.10	0.15	0.70	1.32
2	0.72	0.39	0.53	2.32	5.28
3	1.81	1.01	0.81	8.30	8.48
4	2.50	1.57	0.91	8.55	8.56
6	6.22	7.90	7.44	8.66	9.40
8	9.67	9.50	9.35	9.67	9.53
10	9.82	9.72	9.75	9.47	9.50

Relationships among the amount of water stable crumbs, pH of the system during the reaction and amount of PVA added to clay are illustrated in Figure 4.12.

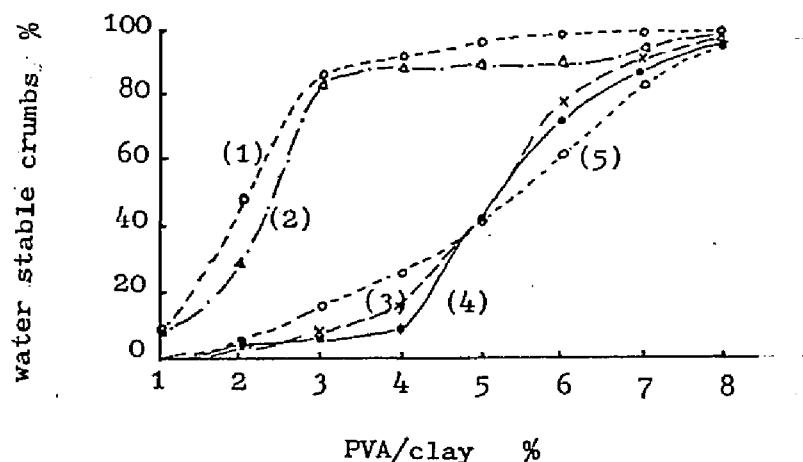


Figure 4.12 Effects of pH on water stability of complexes where pH of medium during the reaction of PVA-Bent of complex presenting curves 1, 2, 3, 4 and 5 are 2.15, 3.90, 4.60, 6.30 and 7.00, respectively.

Curves in Figure 4.12 are divided into two groups according to their modes, i.e. curves 1 and 2 belong to group 1 and other three curves to group 2. Curves in group 1 show that complex in this group has about complete water stable character when 4 % of PVA is added, while complex of group 2 gets the complete water stability when 8 % of PVA is added to clay.

As mentioned in the former paragraph, the difference of water stable character of these two groups is inferred as the difference of the state of molecules adsorbed onto clay surface.

In order to examine this inference, X-ray diffraction analyses

of those complexes were conducted. Some of X-ray diffraction diagrams for complexes belong to these two groups are illustrated in Figures 4.13, 4.14 and 4.15.

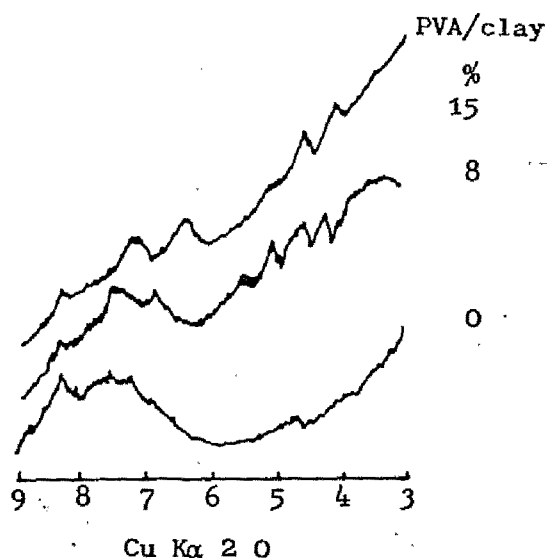


Figure 4.13 X-ray diffraction diagrams of the complex formed under the pH of 2.15

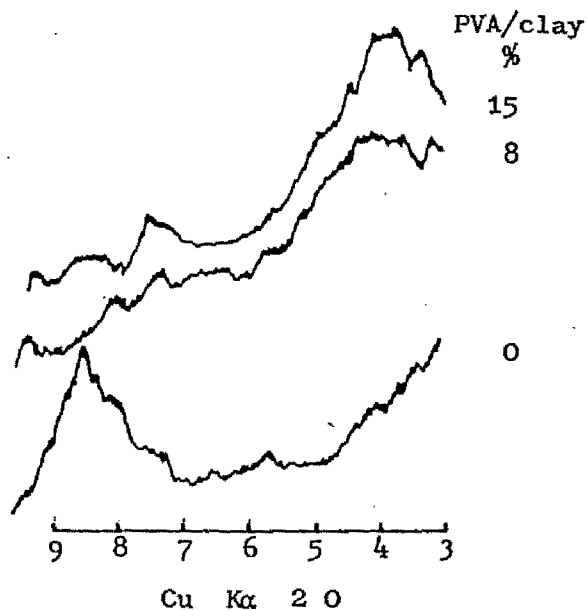


Figure 4.14 X-ray diffraction diagrams of the complex formed under the pH of 3.90.

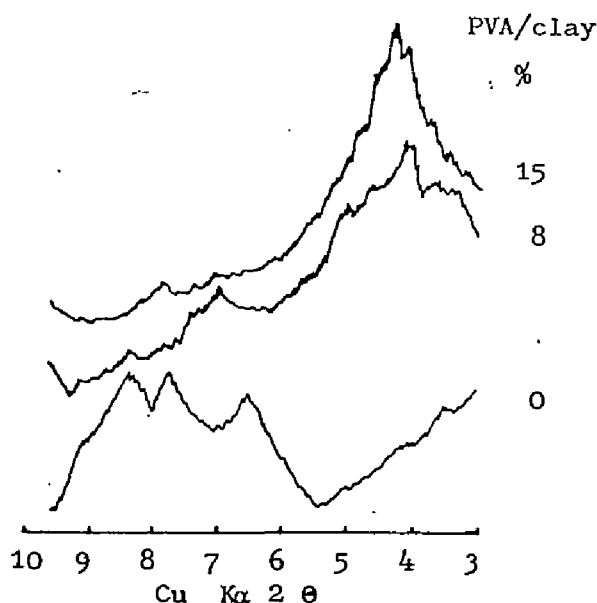


Figure 4.15 X-ray diffraction diagrams of the complex formed under the pH of 4.60.

Curves of Figure 4.13 suggest that some of polymer molecules are adsorbed onto intercrystalline lattice surface of montmorillonite though the degree of orientation of adsorbed polymer molecules is low. So the most of PVA added to clay are supposed to be adsorbed on outer surface of clay. On the other hand, Figure 4.15 shows that polymer molecules are adsorbed onto intercrystalline surface of montmorillonite regularly, but curves in Figure 4.14, which belongs to group 1, show the intermediate mode of curves in other two Figures.

The difference between water stability of complexes formed under different pH of mediums could not be explained as only the difference of the state of PVA molecules adsorbed onto clay surface, though this factor seems to play main role on water stability.

In the former paragraph it was assumed that force acting to break up of crumbs is constant, but this assumption brings some inconsistency into the explanation on water stability of complexes through

X-ray diffraction diagrams in above Figures.

But this inconsistency is immediately solved when one realizes that the expansible force of montmorillonite is decreased by treating with HCl. But this explanation involves some of inference, so to examine the inference the expansibility of complexes was measured.

The index used for the degree of expansion of a complex is shown as follow;

$$D.E. = \frac{\text{Amount of crumbs more than 4 mm in size}}{\text{Amount of crumbs more than 2 mm in size}} \cdot 100$$

Relationships between the degree of expansion of complexes and pH under which complexes were prepared are illustrated in Figure 4.16.

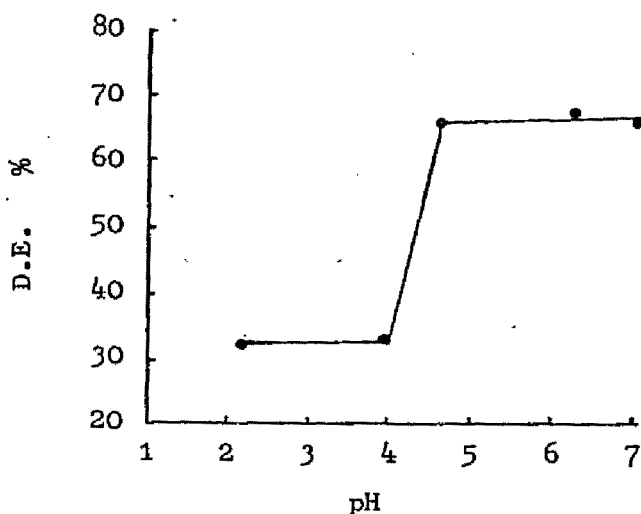


Figure 4.16 Degree of expansibility of complex formed under various pH of solution.
where values of the degree of expansion are mean value of complexes involving 8 and 10 % of PVA.

Figure 4.16 shows that difference of the degree of expansion between complexes formed under pH of 3.90 and 4.60 is clearly.

Curves in Figure 4.14 show that this low expansibility of the complexes was obtained through the process of drying, for PVA molecules are adsorbed onto intercrystalline surface of montmorillonite.

iii. Effects of the exchangeable cations

It was clarified that the surface area available to adsorption of Ca-Bent is less than that of Na-Bent, and it has been well known that expansibility of calcium montmorillonite in water is inferior to that of sodium montmorillonite. So it is expected that water stability of PVA-Na-Bent complex will be somewhat different from that of PVA-Ca-Bent one. On the other hand, effects of pH of the medium on water stability of complex may be explained clearly from the studies on water stable characters of PVA-Ca-Bent complex.

Distribution of water stable crumbs after test of PVA-Ca-Bent complex is tabulated in Table 4.7.

Table 4.7 Distribution of water stable crumbs of Ca-Bent complex
Sample used 2-4 mm 10 g.

PVA/clay %	Distribution of crumbs (g.)		
	4 mm	4 - 2 mm	2 - 0.5 mm
1	0.20	2.90	5.24
2	0.54	7.15	1.82
3	4.68	4.70	0.29
4	5.77	3.81	0.16
6	6.46	3.04	0.12
8	5.12	4.40	0.15
10	6.52	3.09	0.09

A relationship between amount of water stable crumbs and PVA added to clay are presented in Figure 4.17.

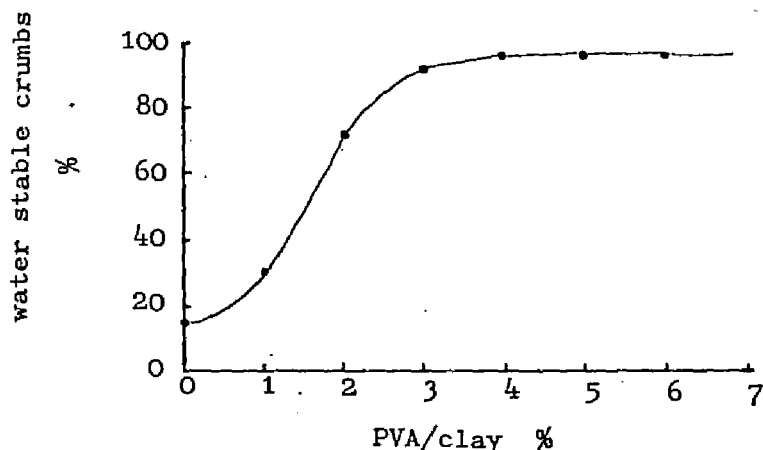


Figure 4.17 Water stability of PVA-Ca-Bent complex

This Figure shows that the complex gets complete water stable character when only 3 % of PVA added to clay. This fact suggests that if the most of PVA added were adsorbed onto only outer surface of montmorillonite and expansibility of montmorillonite were not so large, 3 % of PVA would be enough to make the complex complete water stable one.

In order to examine the effects of expansibility of montmorillonite the exchangeable cation of PVA-Ca-Bent complex was exchanged for sodium ion by washing with N-NaCl solution.

After drying, the exchanged complex was offered to water stability test. Results of the test are illustrated in Figure 4.18.

This figure shows that if all of added PVA were adsorbed onto only outer surface of montmorillonite and clay had large expansibility, 4 % of PVA would be necessary to make the complex complete water stable.

Relationships of water stability of complex and pH of the medium under which the complex was prepared are discussed from the results of Figure 4.18

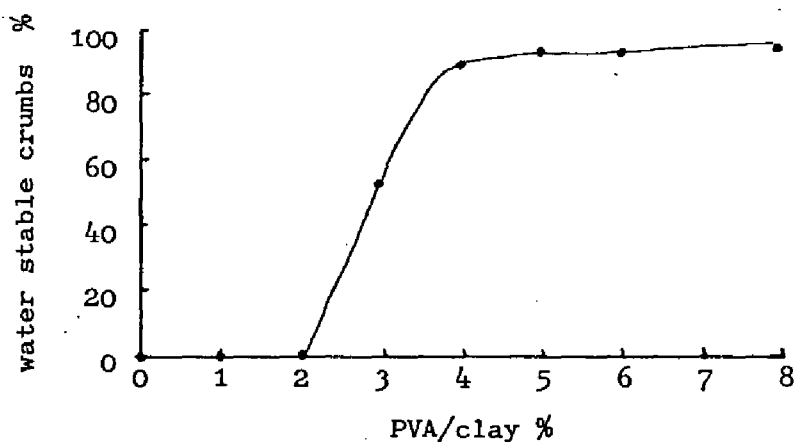


Figure 4.18 Water stability of PVA-Ca-Bent exchanged complex

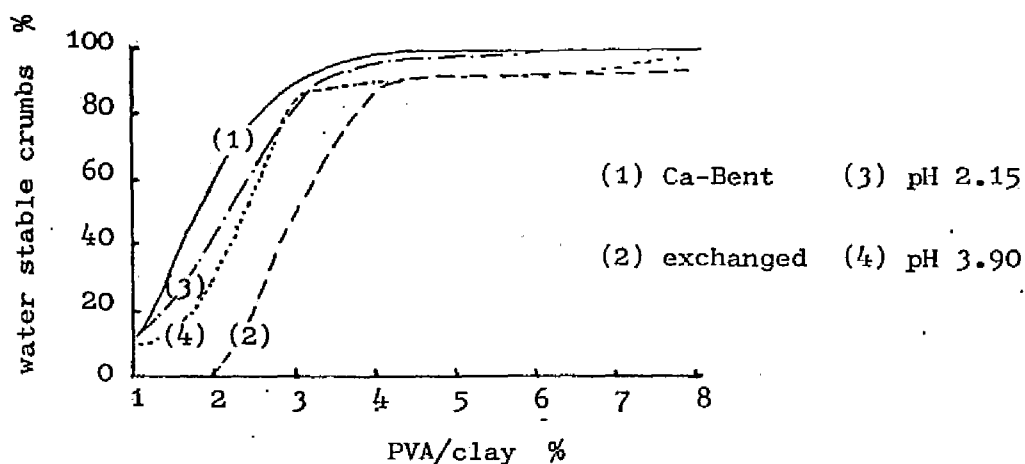


Figure 4.19 Comparision of water stability of some complex.

In Figure 4.19 , are illustrated curves in this Figure and those of Figure 4.12.

Comparing these four curves, the resemblance of their modes suggests the mechanisms of water stability of complexes formed lower pH region are the same as those of PVA-Ca-Bent complexes.

iv. Summary

Results obtained in this Chapter are summarized as follow;

Water stability of complex is affected by the amount of polymer adsorbed on clay surface and the state of polymer molecules in the complex, especially polymer adsorbed onto outer surface of montmorillonite plays an important role on water stability of the complex.

Water stability of a complex is affected by pH of the medium during the reaction of PVA and montmorillonite. The higher the concentration of hydrogen ion of the medium, the less the amount of PVA needed for making the complex complete water stable becomes.

If all polymer molecules added were adsorbed onto only outer surface of sodium montmorillonite, the complex formed would get complete water stability when 4 % of polymer was added to the clay.

CHAPTER 5

KINETICS OF THE THERMAL DEGRADATION OF POLYVINYL ALCOHOL IN MONTMORILLONITE COMPLEX

Polymers added to clay and adsorbed onto clay surface alter physical and chemical properties of clay surface, some changes in those characters were discussed in Chapter 4 in relation to water stability of Bentonite treated with polyvinyl alcohol.

On the other hand, being adsorbed onto clay surface, some characters of polymer molecules seem to be altered to some extent. If one will be able to detect those changes in polymer molecules it may be possible to differentiate polymers in the complex according to their existing states.

It is apparent that there are two existing states of PVA molecules in the dried PVA-Mont complex. Parts of molecules are bound directly to clay surface, the other parts of molecules are in free state.

Quantitative acknowledgements about the amount of adsorbed parts and free parts of polymer molecules would offer the means to know some relationships between polymer added to clay and the changes in the characters of clay. It is very important to control the characters of polymer-clay system.

There would be many properties of polymer molecules which might be changed by being adsorbed to clay surface, but a focus was put on the changes in kinetics of the thermal degradation of polymer in the system.

The kinetics of reaction were evaluated from the resulting curves by the method of Freeman and Carroll²⁵⁾.

Here the outlines of the method will be presented as follow;

Now consider a reaction, in the liquid or solid states, where one of the products B is volatile and all other substances being in the condensed state.

This is expressed as follow ; $aA = bB + cC$

The rate expression for the disappearance of reactant A from the mixtures is

$$-\frac{dX}{dt} = k X^x \quad (1)$$

where X: amount of reactant, k: specific rate
x: order of reaction with respect to A.

The specific rate is expressed as equation (2)

$$k = Z e^{-E^*/kT} \quad (2)$$

Solving for k in (1) and substituting (2) for k gives equation (3)

$$Z e^{-E^*/kT} = \frac{-(dX/dt)}{X^x} \quad (3)$$

where Z: frequency factor, E^* : energy of activation,
R: gas constant, T: absolute temperature.

The logarithmic form of equation (3) is differentiated with respect to dX/dt , X and T, resulting in equation (4)

$$\frac{-E^* dT}{R T^2} = d \ln (-dX/dt) - x d \ln X \quad (4)$$

Integrating the above relationship gives equation (5)

$$-\frac{E^*}{R} \Delta \left(\frac{1}{T} \right) = \Delta \ln (-dX/dt) - x \ln X \quad (5)$$

Dividing (4) and (3) by $d \ln X$ and $\ln X$, respectively, one obtains equation (6) and equation (7)

$$\frac{E^* dT}{R T^2 d \ln X} = \frac{d \ln (-dX/dt)}{d \ln X} - x \quad (6)$$

$$\frac{-E^*/R \cdot \Delta \left(\frac{1}{T} \right)}{\Delta \ln X} = \frac{\Delta \ln (-dX/dt)}{\Delta \ln X} - x \quad (7)$$

from equations (6) and (7), it is apparent that plots of

$$\frac{dT}{T^2 \log X} \quad \text{vs.} \quad \frac{d \log (-dX/dt)}{d \log X}$$

and

$$\frac{\Delta (1/T)}{\Delta \log X} \quad \text{vs.} \quad \frac{\Delta \log (-dX/dt)}{\Delta \log X}$$

should result in stright lines with slopes of $-E^*/2.3 R$ and intercepts of $-x$. So from the slopes and intercepts, the energy of activation and the order of reaction are gained, respectively.

5.1 Materials and methods

Materials

Three samples of PVA-Mont complex were used besides the mixture of PVA and clay, they are listed up in Table 5.1.

Table 5.1 Samples used

Sample	PVA/clay %	amount of water added during reaction (ml/gram.clay)
A	8	8
B	8	20
C	10	20
D	10	0 (mixture)

Experimental methods

Changes in sample weight were followed by means of Shimazu model 2 thermobalance which was modified for electronic recording.

300 mg of sample was placed in Pt-dish and heated at a rate of 10 °C/min. from room temperature to approximate 600 °C.

Temperature measurements were made with chromel-alumel thermocouple located 0.5 cm above the dish.

Experiments were conducted in air atmosphere.

Changes in weight of sample was recorded as a function of temperature by X-Y recorders.

5.2 Results

Figure 5.1 is a graph of weight loss as a function of temperature for the thermal degradation of 300 mg of PVA-Mont complex A.

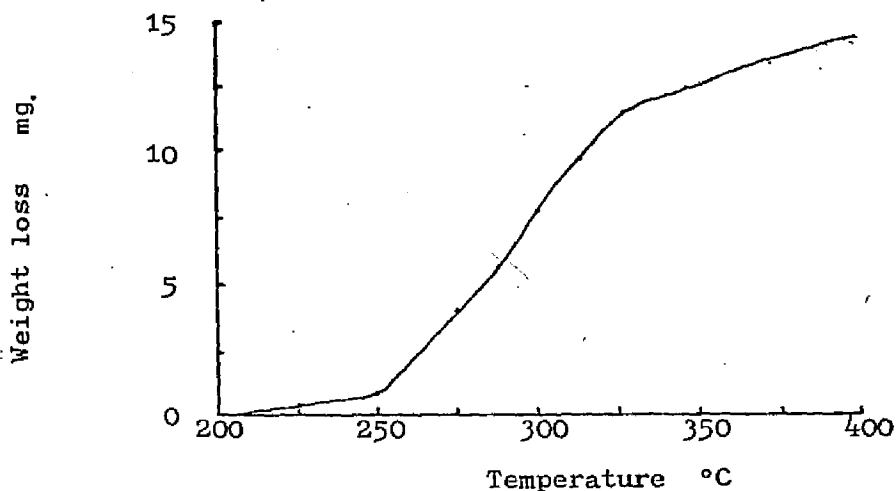


Figure 5.1 Weight loss of complex as a function of temperature.

Figure 5.1 shows that the degradation of PVA began at approximately 270 °C and was relatively rapid in the temperature range 290-310 °C. Figure 5.2 is a graph of rate of weight change as a function

of temperature. There are two stages of reaction as indicated by the band structure of the curve in this Figure.

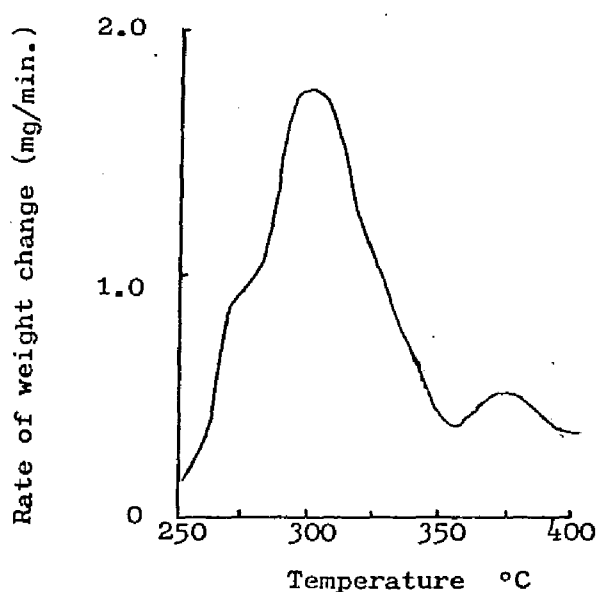


Figure 5.2 Rate of weight change as a function of temperature (A).

The first reaction occurs over the temperature interval of 270 to 340 °C and the first reaction and second one are apparent in this Figure.

Rates of changes in weight of other three samples are illustrated in Figure 5.3.

Curves B and C in this Figure show the analogous mode with curve in Figure 5.2, but the mode of curve D is somewhat different from these of other curves, in sample D the reaction occurred in the temperature range of 350 to 410 °C.

The difference of temperature of thermal degradation of these samples seems to show the difference of the existing states of polymers in the complexes.

Kinetics of main thermal degradation were evaluated from the derivative thermogravimetric curves shown in Figures 5.2 and 5.3

by the method of Freeman and Carrol explained before. The equation used was

$$\frac{\Delta \log (dX/dt)}{\Delta \log X} = x - \frac{E^*/2.3 R \Delta (1/T)}{\Delta \log X}$$

where dX/dt : rate of change in weight, X : weight of reactant at any time, E^* : energy of activation, R : gas constant, T : absolute temperature, x : order of reaction.

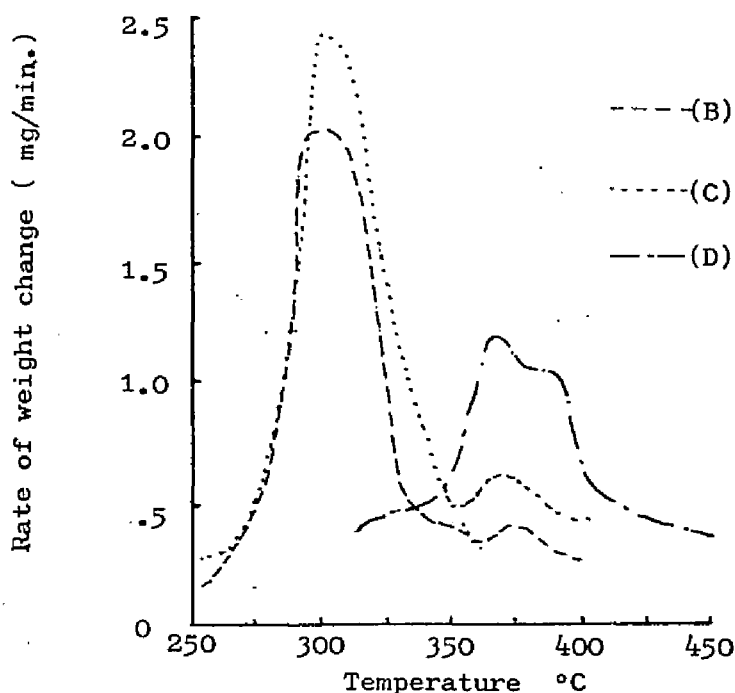


Figure 5.3 Rate of weight change as a function of temperature
(B, C, and D)

Figure 5.4 is a graph of $(\Delta \log dX/dt) / \Delta \log X$ vs.
 $\Delta(1/T) / \Delta \log X$.

For the degradation of PVA in the complex, the linear relationship of these factors shows that the main reaction is uniform chemical reaction. From the intercepts and slopes of each curves, the values of the order of reaction and the energy of activation for decomposi-

tion of PVA in each samples were calculated.

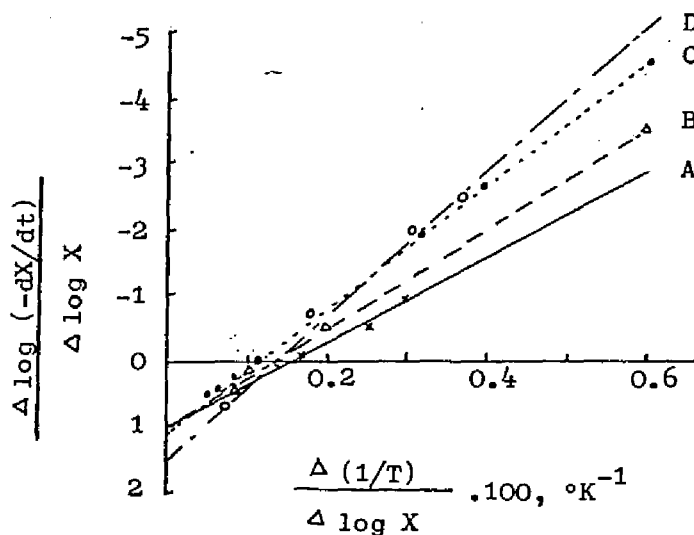


Figure 5.4 Kinetics of the thermal degradation of complex and mixture of PVA and Na-Bent.

Results of calculation are tabulated in Table 5.2.

Table 5.2 Kinetics of thermal degradation of PVA in the complex and in mixture with Na-Bent.

Sample	order of the reaction	energy of activation
	x	E* (K cal/mol)
A	1.15	31.0
B	1.05	32.9
C	1.15	43.1
D	1.50	50.5

Table 5.2 shows that the order of reaction of the thermal degradation of PVA in free state is about 1.6 while that of PVA adsorbed on clay surface is about 1.0.

5.3 Discussions

Grassie³⁴⁾ reported that the thermal degradation of vinyl-compounds are divided to two types by the sorts of reaction products. One type is the reaction in which the reaction product has the same experimental formula with the original polymer, and the other is the reaction in which the product has a different experimental formula from that of the original polymer.

Polyethylene, polystyrene and polymethacrylate belong to the former type and polyvinyl alcohol, polyvinyl acetate and polyvinyl chloride belong to the latter type.

Yamaguchi¹⁰⁴⁾ and Imai⁵⁰⁾ studied about the reaction products of the thermal degradation of PVA and Imai suggested that the products of the thermal degradation of PVA would be acetaldehyde, acetone-phenone, organic acids, crotonaldehyde, hexadien, octatrienal, benzaldehyde, phenole compounds etc.:

Thinking from the order of reaction of the thermal degradation of PVA in the complex, the reaction of degradation of PVA adsorbed on clay surface and that of PVA in free state are inferred to be different in each reaction.

The order of reaction of thermal degradation of PVA adsorbed on clay is 1.0 so reaction products would be not so complex. This inference would be supported by the linear existing state of PVA molecules adsorbed on clay surface.

While the order of the reaction of PVA in free state takes about 1.6 and it suggests that the reaction products would be somewhat complex. PVA in free state would take in unstretching and coiling form, and from these existing state complex compounds would be produced.

Activation energy of thermal degradation of PVA adsorbed on clay

surface is 31 Kcal/mol and that of PVA in free state is 50 Kcal/mol.

The reason why the activation energy of thermal degradation of PVA adsorbed on clay surface is lower than that of PVA in free state is supposed to be the difference of the existing state of PVA molecules in the sample.

As mentioned before PVA molecules in free state have the coiling form and so degree of freedom of movement around C-C bonding would not be restricted as in those of adsorbed on clay surface, consequently thermal energy applied would be exhausted as energy of movement of carbon atoms around their bonding axis to some extent, which cause the larger energy of activation of thermal degradation of PVA in free state.

While in PVA adsorbed on clay surface, C-C bonding is stretched to some extent so degree of freedom of movement around the bonding axis would be restricted and thermal energy applied would act as separating force of the bonding without being exhausted to energy of movement of carbon atoms. On the other hand, some catalytic action of clay surface might be worked for the degradation of PVA adsorbed onto clay surface.

Energy of activation of thermal degradation of sample C is 41 Kcal/mol and order of reaction is about 1.2.

These values are explained as follow; sample C involves both PVA molecule in free state and adsorbed on clay surface, so each values takes the middle of that for samples A and D.

Utilizing these results, it seems to be possible to analyse quantitatively PVA in free state and those adsorbed on clay surface in a complex.

It is difficult to analyse them from thermal gravimetric curves, for the degradation products of PVA might be adsorbed onto clay surface.

Quantitative analysis of PVA in a complex will be conducted by differential thermal analysis.

5.4 Summary

Kinetics of thermal degradation of PVA in the PVA-Mont complex and in mixture with clay were studied..

Energy of activation of thermal degradation of PVA in free state and that adsorbed on clay surface are 50 Kcal/ mol and 31 Kcal/mol, respectively.

Order of reaction for thermal degradation of PVA in free state and adsorbed on clay surface are 1.6 and 1.0, respectively.

CHAPTER 6

DIFFERENTIAL THERMAL ANALYSIS OF POLYVINYL ALCOHOL-MONTMORILLONITE COMPLEX

Results obtained in Chapters 3 and 4 suggested that there would be two different existing states of PVA molecules in the complex, namely PVA molecules adsorbed onto clay surface and those in free state.

Of course the amount of PVA involved in a complex is an important key to clarify physical and chemical properties of the complex, but the amount of PVA in the complex was not enough to explain many phenomena of PVA-clay systems without any inconsistency. More detail analysis of existing states of PVA in the complex will contribute to studying on various phenomena of the system.

The separative analysis of PVA in the complex according to its existing state is necessary to know the properties of the complex dried.

The author intends to determine amounts of PVA in the complex separately according to its existing state. Fortunately, in Chapter 5 some of physical properties of PVA in the complex were clarified to some extent, so analysis of PVA might be done to some detail by using those properties.

Differential thermal analysis (DTA) technique was employed in the determination of the amount of PVA in each states.

Firstly the results of qualitative analysis of PVA-Mont complex will be presented in paragraph 6.2, where the characteristics of DTA curves will be shown. Then experiment will go into the quantitative analysis of the complex and a new method for the separative analysis of PVA in the complex according to its existing state will be proposed.

As the utilization of the new method, effects of the degree of polymerization of PVA on the adsorption onto montmorillonite and a

relation between water stable character of the complex dried and the amount of PVA adsorbed onto clay surface will be discussed.

6.1 Materials and methods

Clay samples used were Na-Bent and Ca-Bent and polymers used were PVA-1, PVA-2, PVA-3 and PVA-4.

Preparations of PVA-Bent complex

Using these polymers and clays, PVA-Bent complexes were prepared as follow; various amount of PVA was added to a definite amount of clay suspension, then complexes gained were dried at 50 °C. The dried complexes were crushed up to powder of less than 0.1 mm in its particle size.

Differential thermal analysis of the complex

Using Shimazu-model 2 A DTA apparatus, differential thermal analysis of complexes were conducted semi-automatically by rising the temperature of furnace uniformly at 10 °C/ min., and $\alpha\text{-Al}_2\text{O}_3$ powder was used as the reference substance.

6.2 Qualitative differential thermal analysis.

PVA-3, Na-Bent, Ca-Bent and complexes from this polymer and clays were offered to differential thermal analysis.

DTA curves for PVA powder are illustrated in Figure 6.1.

These curves are characterized by four endothermic peaks in temperature range of 110 to 400 °C.

According to the process of the thermal degradation of PVA molecules mentioned in Chapter 5, these four peaks and exothermic peaks over the temperature range of 400 °C seem to be responded to the following reactions; The first endothermic peak at 130 to 150 °C seems to be owing to dehydration of free water molecules in the sample. The second and third peaks at 200 and 260 °C are supposed to be owing to dehydration of water molecules combined firmly to clay surface by hydrogen bonding and dehydration among hydroxyl groups of PVA molecules. The fourth endothermic peak at 350 to 360 °C is due to the breaking down of carbon to carbon bonding in

PVA molecules.

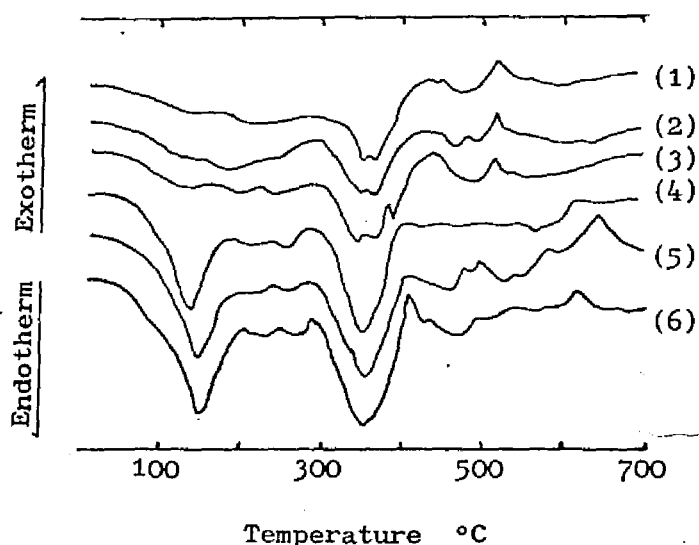


Figure 6.1 DTA curves for PVA

where curves 1, 2 and 3 were gained from the sample in which 30 mg of PVA powder was packed between two layers of alumina powder, and curve 4, 5 and 6 from 60 mg of PVA powder only, respectively.

Burnning of some degradation products of PVA is apperared as the exothermic peaks over 400 °C. The reproducibility of these exothermic peaks was low and it would be due to air content of samples. The regulation of air content in samples was very difficult in this experiment and discussions about those exothermic peaks will not be done in this experiment.

DTA curves of Na-Bent and the mixture of PVA and Na-Bent are presented in Figure 6.2.

Curve 7 (Na-Bent) has an endothermic peak at 150 °C and a shoulder at 170 °C. There is no other thermal reaction over the temperature range of 200 to 500 °C and this fact will have an important meaning

in the analysis of DTA curves. Other two curves have two endothermic peaks at 150 and 350 to 360 °C. The former peak is the same as shown in curve 7 in this figure and the latter one is the same peak as shown in curves in Figure 6.1.

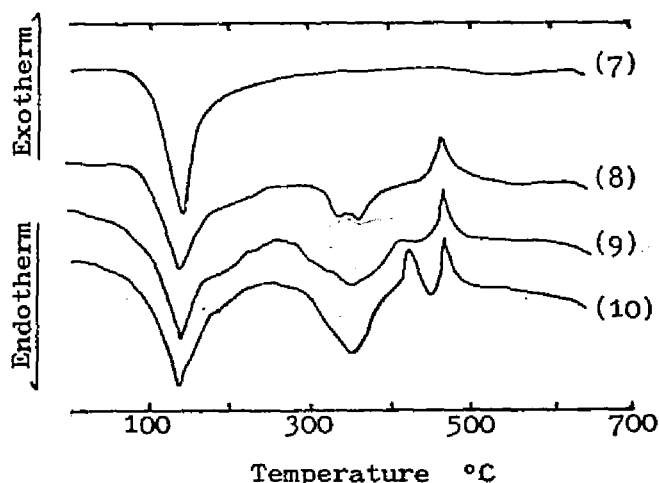


Figure 6.2 DTA curves of Na-Bent and mixture of PVA and Na-Bent where curve 7 was obtained from Na-Bent and other curves were gained from mixture samples.

In Figures 6.3 and 6.4 are illustrated curves for complexes of PVA and Na-Bent. Amount of PVA added to clay in each sample is listed up in Table 6.1.

The most conspicuous feature of these DTA curves of complexes is the endothermic peak at about 270 °C, which did not be observed in curves of PVA and mixture of clay and PVA.

It is also noticeable that the area of these endothermic peak becomes larger with increasing of the amount of PVA added to clay.

The exothermic peaks observed over the temperature range of 400 °C

do not be discussed in this experiment because these peaks could not be got as reproducible forms.

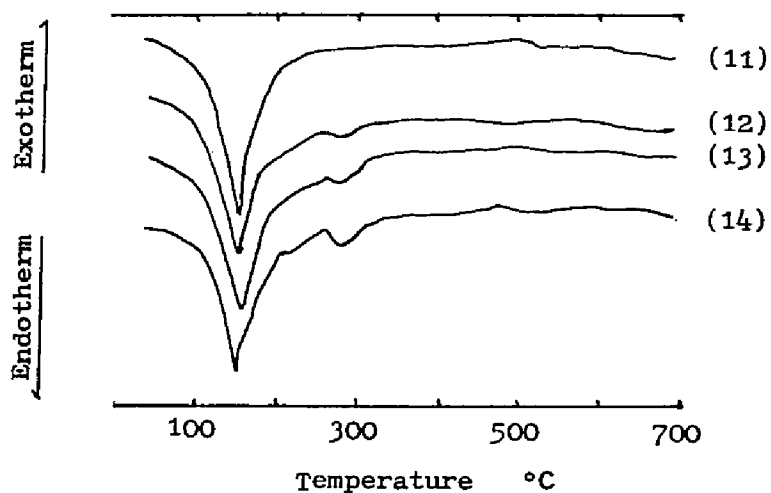


Figure 6.3 DTA curves of PVA-Na-Bent complex

Table 6.1 Amount of PVA added to clay to make complex.

Curve No.	PVA/clay %	Curve No.	PVA/clay %
11	2	15	8
12	3	16	9
13	4	17	10
14	6	18	20

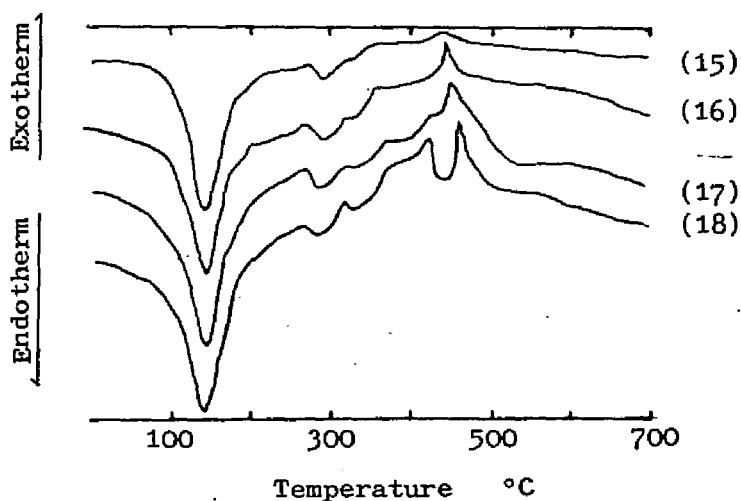


Figure 6.4 DTA curves of PVA-Na-Bent complex

DTA curves of Ca-Bent and PVA-Ca-Bent complexes are illustrated in Figures 6.5 and 6.6 and the ratio of PVA added to clay are tabulated in Table 6.2.

Table 6.2 Ratio of PVA added to clay to make complexes

Curve No.	PVA/clay %	Curve No.	PVA/clay %
1	0	5	6
2	2	6	10
3	3	7	12
4	4	8	14

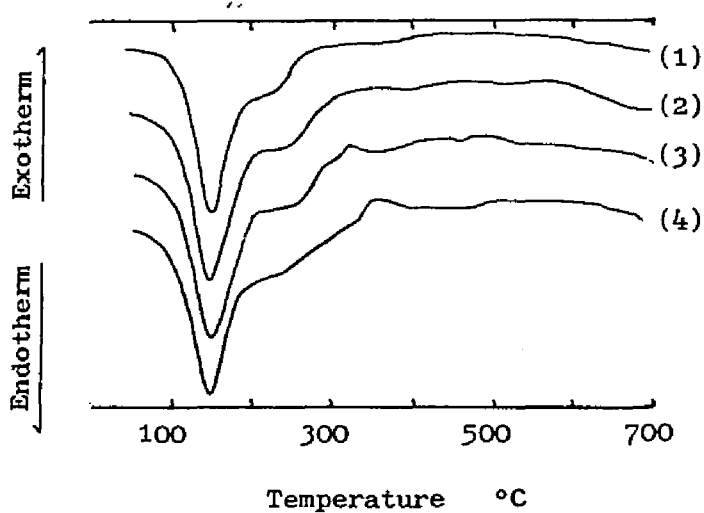


Figure 6.5 DTA curves of Ca-Bent and PVA-Ca-Bent complexes

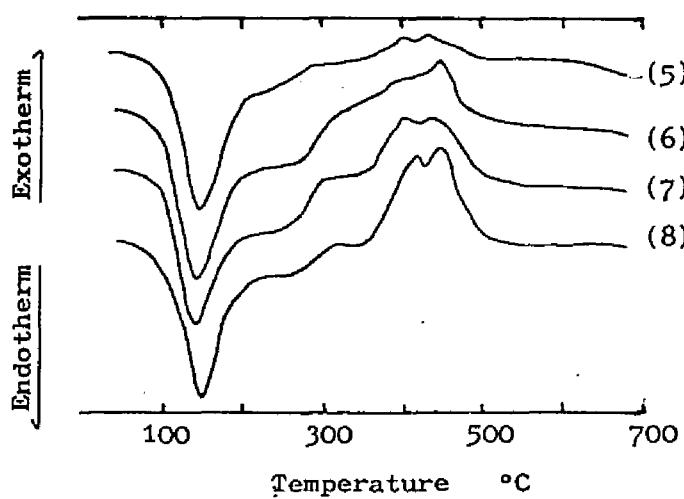


Figure 6.6 DTA curves of Ca-Bent-PVA complexes.

Curve for Ca-Bent has two characteristic endothermic peaks at 150 °C and 230 to 240 °C. Curves for PVA-Ca-Bent complexes have analogous peaks, but endothermic peaks are also observed in curves of higher polymer content. The endothermic peak at 270 °C dose not be found in these curves of the complexes.

The discussions of the results obtained in this paragraph will be given.

As shown in Figure 6.1, DTA cuves for PVA in free state are characterized by four endothermic peaks and one exothermic peak.

The first endothermic peak at 150 °C is due to dehydration of water in free state and the second and third peaks are attributed to the dehydration of water in hydrogen bonding with clay surface and the dehydration of inter molecular OH groups in PVA. The fourth endothermic peak is due to the breaking down of C-C bondings in PVA. The exothermic peak over the temperature range of 400 to 520 °C are attributed to the combution of the compounds produced through the thermal degradation of PVA molecules.

Comparing curves of PVA and those of mixtur in Figure 6.1, there are no noticeable differences among those curves.

Here it is concluded that C-C bonding of PVA in free state is broken down at 350 to 360 °C and this process is appeared as an endothermic peak at this temperature.

Endothermic peak at 270 °C in curves for PVA-Na-Bent complexes is infered to be due to the breaking down of C-C bonding of PVA adsorbed on clay surface, which is supported by the facts obtained in Chapter 5.

The reason why the temperature of the breaking down of C-C bonding in PVA adsorbed on clay surface is lower than that of in free state was mentioned in Chapter 5.

Here a possibility of analysis of PVA according to its existing state seems to be born from DTA curves of complexes.

The mode of DTA curve of Ca-Bent is somewhat different from that of

Na-Bent, i.e. in the former curve an endothermic peak is observed at 230 to 240 °C, while the latter has no such peak at the same temperature. This endothermic peak seems to be due to dehydration of water molecules hydrated to calcium ions.

One can not observe the peak due to the breaking down of PVA adsorbed on clay surface at 260 to 270 °C. It is supposed that this peak would be shifted to lower temperature range by combining with the peak due to dehydration of water hydrated to calcium ions.

From these DTA curves of PVA-Bent complexes, it is inferred that breaking down of PVA in free state is appeared as an endothermic shoulder over the temperature range of 310 °C, which are observed in curves of complexes involving large amount of PVA.

6.3 Quantitative differential thermal analysis

The difference of characters of PVA adsorbed on clay surface and in free state were clarified in the former paragraph. Using this difference, the author intends to analyse PVA in the complexes according to its existing states. The fundamental theory in relation to the quantitative analysis of PVA in the complexes according to its existing states will be presented below.

i. Theory

The sample holder used in this experiment is shown in Scheme 6.7.

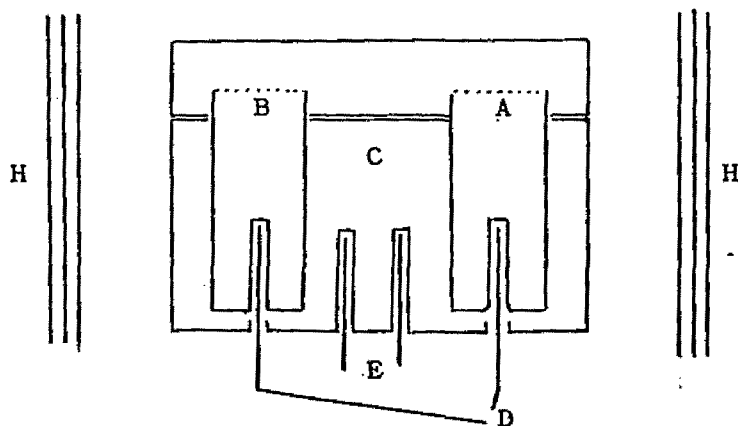
In the right hand cell (A), sample is placed and the heat stable substance, α -alumina, is placed in the left hand cell (B).

The temperature of the sample is raised by a heater (H) and heat is assumed to be transferred by conduction alone through sample holder (C). The temperature of the sample as well as the temperature difference between two cells is measured as a function of time, the temperature difference is measured by thermal couple (D) and the temperature of the sample holder is measured by the thermo couple (E).

T_A , T_B and T_C are the temperature of the sample, reference substance and the sample holder, respectively.

The condition of uniform temperature in cell cannot be met exactly

by solids, but when the diameter of sample cell is small, the condition of uniform temperature is assumed to be attained approximately.



Scheme 6.7 Sample holder

Generally the changes in heat content of substance is represented by the equation (1)

$$C_p dT = dq_p \quad (1)$$

where C_p is the total heat capacity of the substance, dq_p is the heat transferred to the substance and dT is the temperature in the substance.

The same relationship as shown in equation (1) is assumed to be hold in the sample (A), the relationship of equation (2) is obtained.

$$C_{pA} dT_A = dH + K_A (T_C - T_A) dt \quad (2)$$

where C_{pA} is the total heat capacity of the sample, dH is the heat evolved by the thermal reaction of the sample and K_A is the heat transfer coefficient of the sample cell, Pt cell.

Equation (2) shows that the changes in enthalpy of the sample ($C_{pA} dT$) is equal to the heat change by the reaction in the sample plus the heat transferred into the sample through sample holder. Similar relationship is hold for the reference but in reference substance the heat change by the reaction is zero, so equation (3) is obtained

$$C_{pB} dT = K_B (T_C - T_B) dt \quad (3)$$

where C_{pB} is the total heat capacity of the reference substance and K_B is the heat transfer coefficient of Pt cell.

The heat transfer coefficient of the sample cells, Pt cells, are the same, so

$$K_A = K_B = K \quad (4)$$

On the other hand, the heat capacities of the sample and reference substance are assumed to be nearly the same in the temperature region of this experiment, which was beared out by the facts that the DTA curves of the clay run on the base line, so equation (5) is gained

$$C_{pA} = C_{pB} = C_p \quad (5)$$

Subtracting equation (3) from equation (2), and the subscripts on C_p and K have been dropped, equation (6) is obtained

$$dH = C_p (dT_A - dT_B) + K (T_A - T_B) dt \quad (6)$$

Now it is assumed that the thermal reaction in the sample begins at the time t_1 and ceases at t_2 , total heat transferred in this time interval is obtained by integration of equation (6) between $t=t_1$ to $t=t_2$.

Using the conventional symbol ΔT for $T_A - T_B$ and assuming C_p and K to be independent of temperature over the interval where the reaction occurs, equation (7) is obtained.

$$H = C_p \Delta T + K \int_{t_1}^{t_2} \Delta T dt \quad (7)$$

Since $d\Delta T$ is zero at both $t=t_1$ and $t=t_2$, the first term of the right hand side of equation (7) becomes zero, so

$$H = K a \quad (8)$$

where a is $\int_{t_1}^{t_2} \Delta T dt$, i.e. the area under the DTA curve.

Equation (8) is shown explanatorily in Figure 6.8.

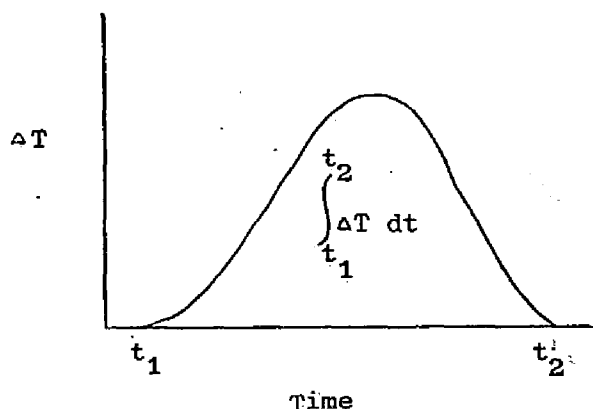


Figure 6.8 Quantitative meaning of DTA curve

On the other hand, it is assumed that the heat changes in a small time interval is directly proportional to the number of moles (dn) reacting during that time, so

$$d h \propto dn \quad (9)$$

$$\text{and} \quad H \propto n \quad (10)$$

where n is the number of moles reacting in the time interval of t_1 to t_2 .

From equation (8) and (10), equation (11) is obtained

$$n \propto a \quad (11)$$

Equation (11) states that number of reactant moles is known from the measurement of the area of exothermic or endothermic peak on the DTA curves.

It is necessary to determine the optimum experimental conditions and the methods to measure the area of the peak in problem for the quantitative analysis of the complexes.

ii. Experimental conditions

Rate of heating

It is desirable for the separative analysis of PVA in the complex to get the peak in the problem isolately. It has been well known that the temperature at which a peak is appeared is influenced by the rate of heating, so relations between the rate of heating and the temperature of peaks in the problem should be clarified for the above purpose.

Table 6.3 shows that relations between the temperature of endothermic peaks due to the breaking down of C-C bondings in PVA molecules adsorbed on clay surface and in free state.

This Table suggests that the optimum rate of heating for this

experiment would be 10 °C/min..

Table 6.3 Temperature of endothermic peaks and rate of heating

Rate of heating °C/min.	Temperature of endothermic peak °C		ΔT ($T_f - T_a$) °C
	PVA in free state T_f	PVA adsorbed T_a	
2	330	280	50
10	370	285	65
25	370	310	60

Other experimental conditions

In the process of heating, changes in the volume of the samples were often observed and those changes were appeared as noises on DTA curves. The largest change in the volume of sample is due to the dehydration of water in free state. So in order to avoid this change, all samples were predried at 110 °C.

Thus dried samples were packed into the Pt cell under the pressure of 25 kg/cm².

Measurement of peak area

The theory mentioned above shows that a peak area on DTA curve is Proportional to number of moles reacting that temperature, so it is possible to know the amount of reactant from the peak area. One must to know when the reaction begins and when it seases.

DTA curves are examined carefully so as to know these temperature.

The author found that there are two groups of endothermic peak due

to the breaking down of PVA adsorbed on clay surface.

Figure 6.9 presents these two groups.

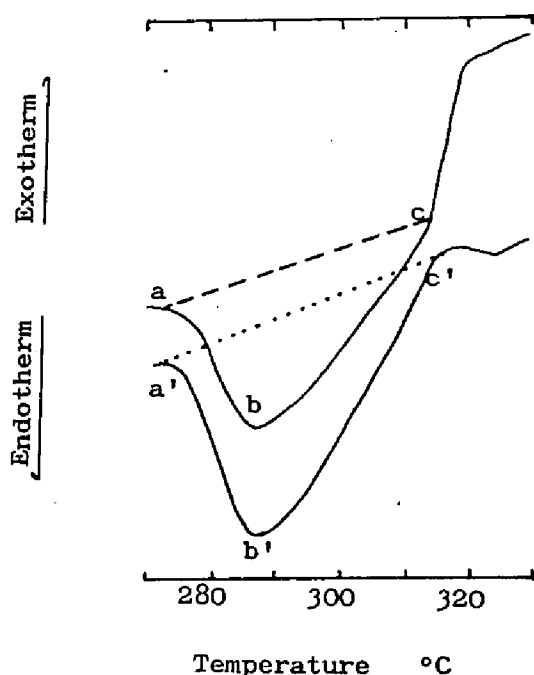


Figure 6.9 Schematic explanation of procedure of measuring of peak area.

Points c and c' in these curves show the end point of a reaction. So the peak area due to PVA adsorbed on clay surface is proportional to the amount of PVA reacting there.

iii. Results and discussions

Determination of the amount of PVA adsorbed on Na-Bent.

DTA curves for PVA-Na-Bent complex are illustrated in Figure 6.10. The area of endothermic peaks measured are tabulated in Table 6.4.

The data of Table 6.4 show high reproducibility of the results of experiment.

In Figure 6.11, are illustrated peak area vs. amount of PVA added to clay. This Figure shows that this curve consists of two parts,

one is a part of straight line, and the other is taking the appearance of curve.

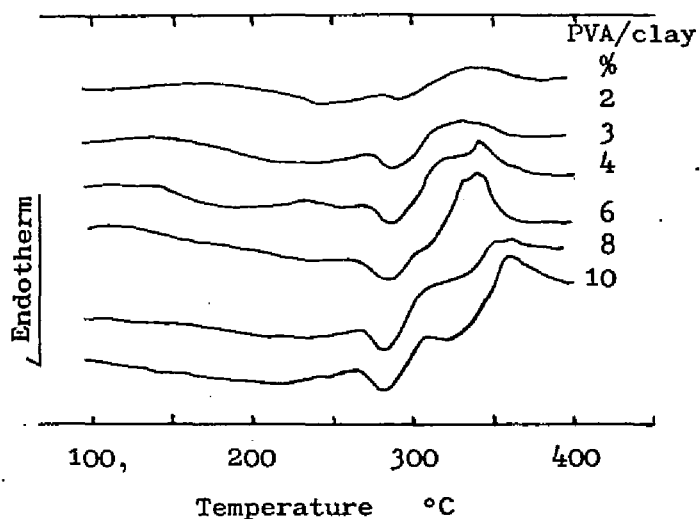


Figure 6.10 DTA curves of PVA-3-Na-Bent complex

Table 6.4 Area of endothermic peak (PVA-3-Na-Bent)

PVA/clay %	Area of endothermic peak, mm ²			mean, mm ²
	1	2	3	
2	47.5	49.5	53.0	50
3	78.0	80.5	75.5	78
4	98.0	101	98.0	99
6	149	147	144	147
8	164	158	163	162
9	168	171	-	169
10	176	179	176	177
20	200	208	-	204

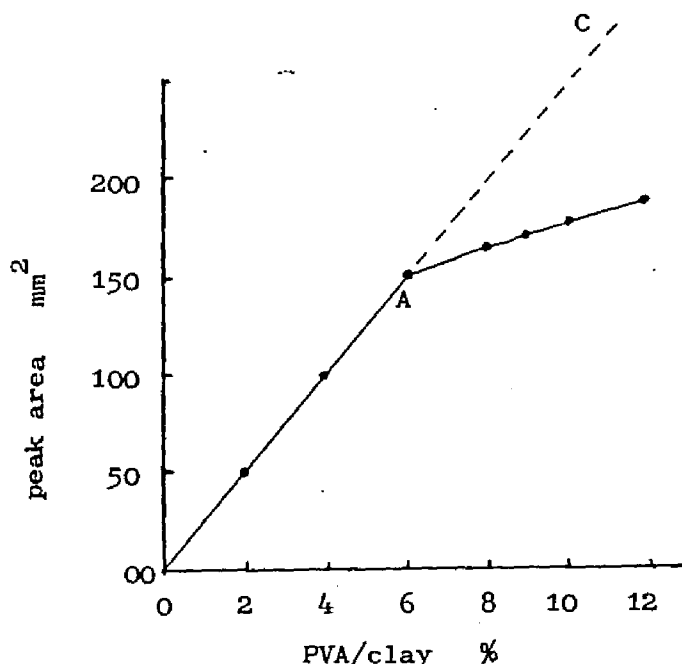


Figure 6.11 Relationship between peak area and amount of PVA added.

The part of the stright line shows that the amount of polymer added to clay is directly proportional to the area of the endothermic peak, namely all of polymer added in this region are adsorbed on clay surface. But over point A, polymer in free state is observed. This point A is shifted along the line OC according to molecular size of polymer.

This point has an important significance in relation to stereo hindrance of polymer molecules for adsorption on clay surface.

Determination of the amount of PVA adsorbed on clay surface and that in free state were done by the procedure shown schematically in Figure 6.12.

As mentioned above, all PVA molecules added are adsorbed onto clay surface in the region of 0 up to A and over A, PVA molecules in free state begin to exist.

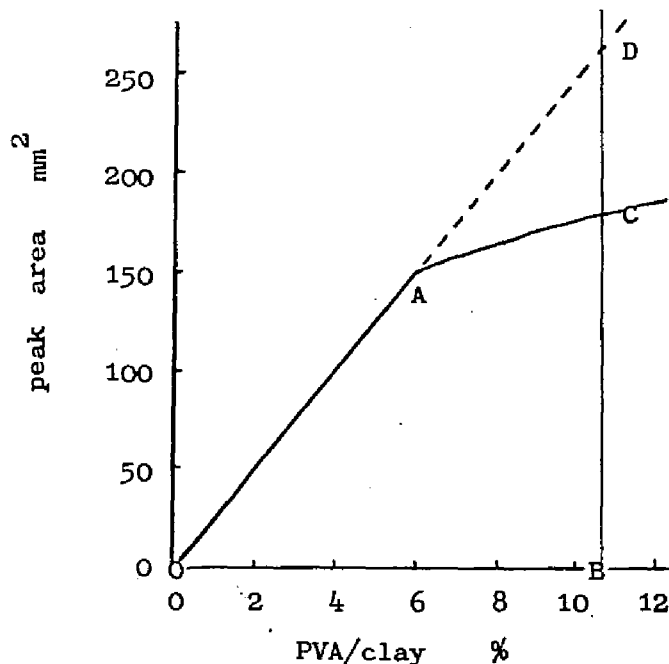


Figure 6.12 Procedure to determining the amount of PVA adsorbed.

Now taking a point B for instance, amount of PVA in two states will be determined. A straight line is drawn perpendicularly to the lateral axis from the point B, and the intersection of this perpendicular line and two upper lines are shown as C and D, respectively.

So amount of PVA adsorbed on clay surface P_a and that of in free state P_f are obtained from equations below;

$$P_a = P \cdot \frac{\overline{BC}}{\overline{BD}} \quad \text{and} \quad P_f = P \cdot \frac{\overline{CD}}{\overline{BD}}$$

where P is amount of PVA added to clay.

Determination of the amount of PVA adsorbed on Ca-Bent surface
Employing the same method as used in the case of Na-Bent-PVA

complex, DTA curves for complexes of PVA-Ca-Bent were obtained. Some of those DTA curves are illustrated in Figure 6.13.

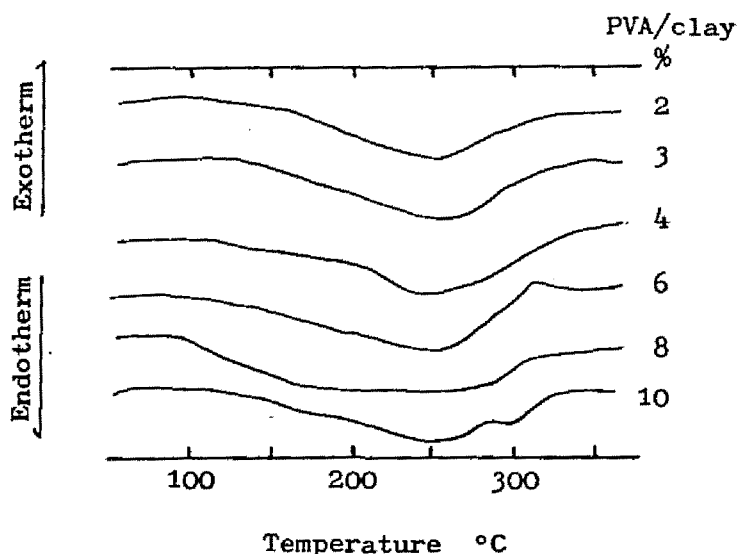


Figure 6.13 DTA curves for PVA-Ca-Bent complexes

Curves in this Figure show no characteristic endothermic peak due to PVA adsorbed on clay surface. It suggests that the dehydration of water hydrated to calcium ions would be incomplete, complete dehydration of those water is difficult under this temperature.

In order to avoid hindrance of calcium ions, the author devised to exchange these ions for sodium ions. This exchange of ions was conducted by washing the complexes with N-NaCl aq. solution and after then with deionized water.

Gained sodium-Bent-PVA complexes were analysed by DTA under the same conditions used other experiment.

DTA curves for these complexes are illustrated in Figure 6.14. Here almost the same mode with Na-Bent-PVA complex is observed.

So the area of endothermic peak were measured. Results of measurement are given in Table 6.5.

Relationship between peak area and amount of polymer added to clay is presented in Figure 6.15.

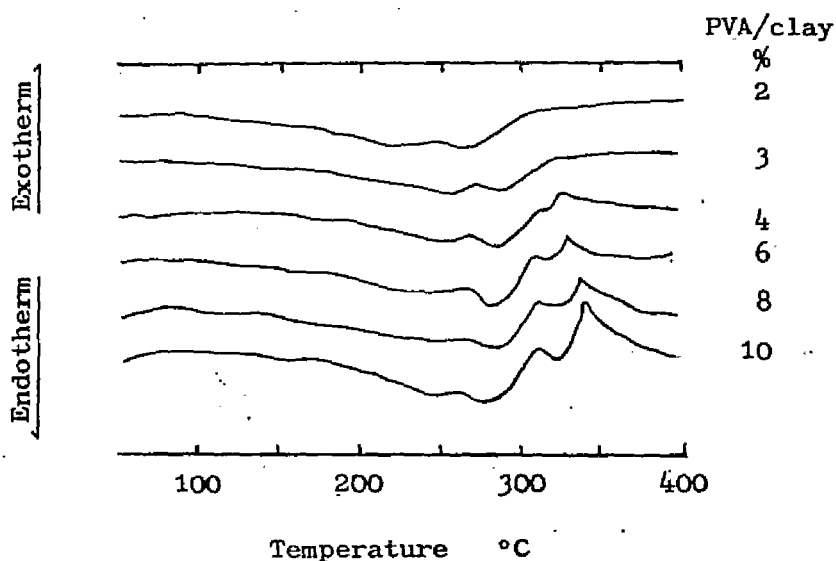


Figure 6.14 DTA curves of cation exchanged complex

Table 6.5 Area of endothermic peak of the cation exchanged complex.

PVA/clay %	Area of endothermic peak, mm ²		mean, mm ²
	1	2	
2	50.0	-	50.0
3	73.3	79.1	76.2
4	94.3	93.5	93.9
6	100	104	102
10	104	110	107
12	112	-	112
14	123	-	123

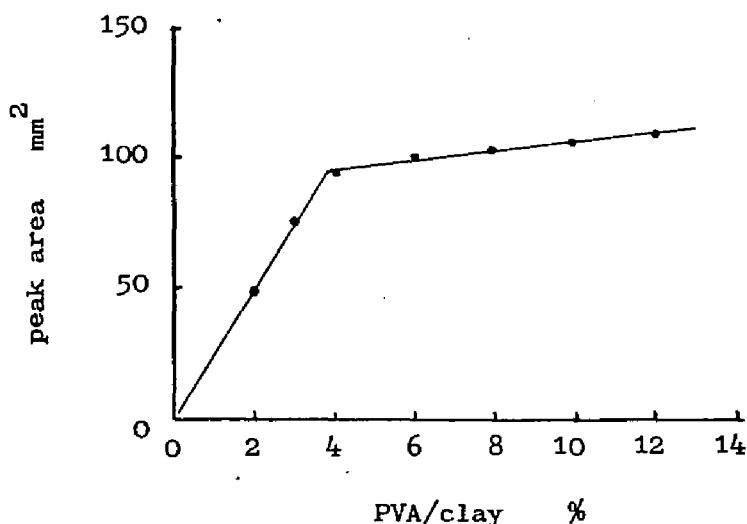


Figure 6.15 Relationship between peak area and amount of PVA added.

From this Figure, one can determine the amount of PVA adsorbed on clay surface and that in free state by using the procedure presented before.

Discussions

Results of determination of amount of PVA in different existing state are tabulated in Tables 6.6 and 6.7.

Table 6.6 shows that all of PVA molecules added to 6 % of clay are adsorbed onto clay surface, over 6 % only a part of remained clay surface are covered with polymer molecules added further.

This fact shows one of remarkable difference between phenomena of adsorption of polymer molecules and small molecules such as ethylene glycol or N_2 gas. In the case of the latter molecules, the hindrance for adsorption appears when all of surface of an absorbent is

covered with adsorbent molecules.

There are many problems in the process of exchanging of cations in the complex. Some changes in the existing states of PVA molecules in the complex are supposed in the process of exchange.

Considering from the stability of PVA molecules adsorbed onto clay surface against washing, the parts of PVA molecules adsorbed onto clay surface would be desorbed through this exchanging process. Of course parts of PVA in free state would be washed out by this process, but they have no effects on the amount of PVA adsorbed on clay surface.

Progressing the exchange of cations, montmorillonite gets expansible characters gradually. It might be occurred that PVA molecules in free state would be adsorbed on inner surface of montmorillonite.

In order to examine this possibility, the ratio of surface covered with polymer molecules to total surface was calculated.

Results of calculation are tabulated in Table 6.8.

Table 6.6 Amount of PVA in different existing state
(PVA-3-Na-Bent)

Ratio of PVA added to clay %	Distribution of PVA in the complex %	
	adsorbed	in free state
6	100	0
8	81.5	18.5
9	73.0	17.0
10	69.0	31.0
20	40.0	60.0

Table 6.7 Amount of PVA in different existing state
(PVA-3-Ca-Bent)

Ratio of PVA added to clay %	Distribution of PVA in the complex %	
	adsorbed	in free state
4	92.5	7.5
6	67.5	32.5
8	50.6	49.4
10	43.0	57.0
12	37.1	62.9

Table 6.8 Ratio of surface covered by PVA to total one
(PVA-3-Ca-Bent exchanged)

Ratio of PVA added to clay %	PVA adsorbed on one gram of clay (g./g.)	Ratio of surface covered with polymer to total surface
4	3.70	94.8
6	4.05	105.3
8	4.05	105.3
10	4.20	109.1
12	4.45	113.0

Data in Table 6.8 were calculated by assuming that polymer molecule could be adsorbed onto only outer surface of montmorillonite in the form of mono-layer. This Table shows that almost all outer surface of montmorillonite is covered with polymer molecules, but it would be impossible to be adsorbed in the same mode with small molecules.

Here this fact suggests that the assumption used in calculation of surface covered by polymer molecules was incorrect.

As mentioned in Chapters 3 and 4, some parts of PVA molecules would be adsorbed on the entrance of intercrystalline lattice of calcium-montmorillonite.

Thus the method to determine the amount of PVA adsorbed on clay surface established by using DTA technique.

6.4 Effects of the degree of polymerization of PVA on the adsorption to montmorillonite

As shown in Figure 6.10, point A has an important significance to stereo hindrance of polymer molecules for adsorption to clay and to the properties of complexes formed. To study the stereo hindrance of polymer adsorption, four sorts of PVA were offered.

Relationship between polymerization of PVA and stereo hindrance of adsorption will be discussed

i. Results

DTA curves for PVA-1-Na-Bent complexes are illustrated in Figure 6.16.

Peak area measured are tabulated in Table 6.9.

Relationship between peak area due to PVA adsorbed on clay surface and amount of PVA added to clay is illustrated in Figure 6.17.

This Figure 6.17 shows that the remarkable stereo hindrance to adsorption appears when 10.35 % of PVA-1 was added to clay.

This value is larger than that of PVA-3.

DTA curves for PVA-2-Na-Bent complexes are presented in Figure 6.18.

Table 6.10 shows results of measurement of endothermic peak area

owing to the degradation of PVA molecules adsorbed on clay surface.

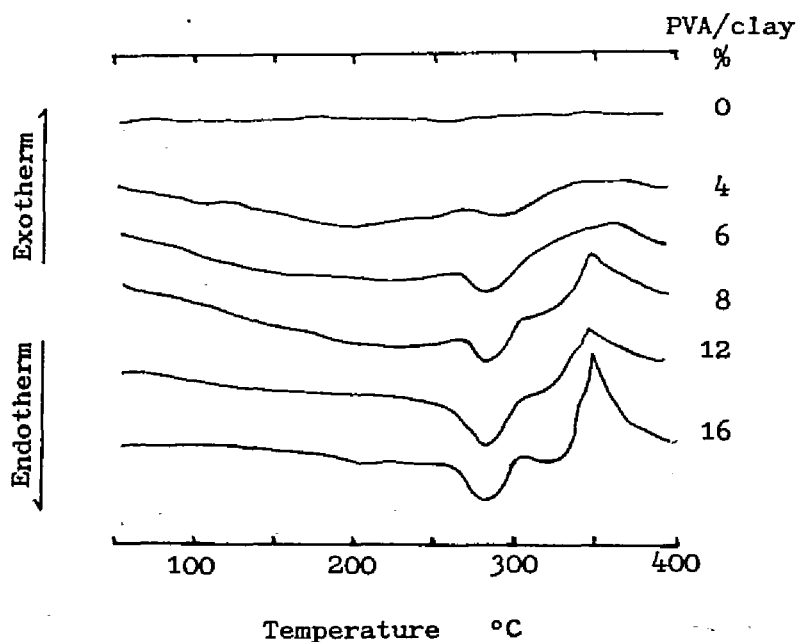


Figure 6.16 DTA curves of PVA-1-Na-Bent complex

Table 6.9 Area of endothermic peak due to PVA adsorbed

PVA/clay, %	Area of endothermic peak, mm ²		mean, mm ²
	1	2	
4	60.0	81.8	70.9
6	128	132	130
8	203	203	203
9	243	245	244
10	272	268	170
12	291	288	289
14	302	301	302
16	315	314	315

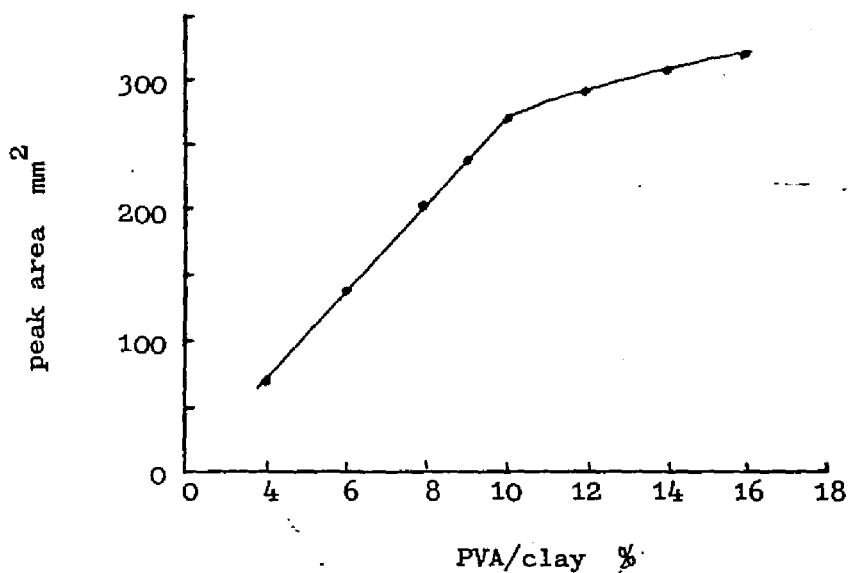


Figure 6.17 Relationship between peak area and amount of PVA added to clay

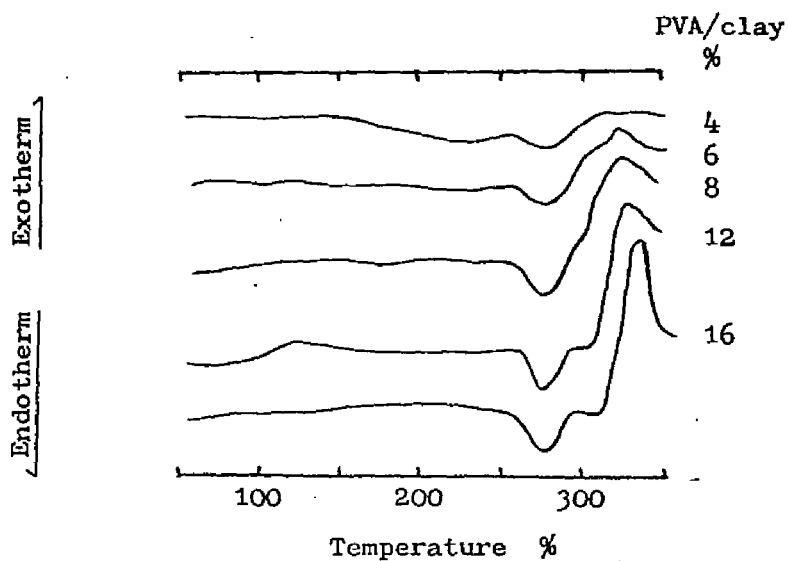


Figure 6.18 DTA curves of PVA-2-Na-Bent complex

In Figure 6.19 are illustrated area of peak vs. amount of PVA added.

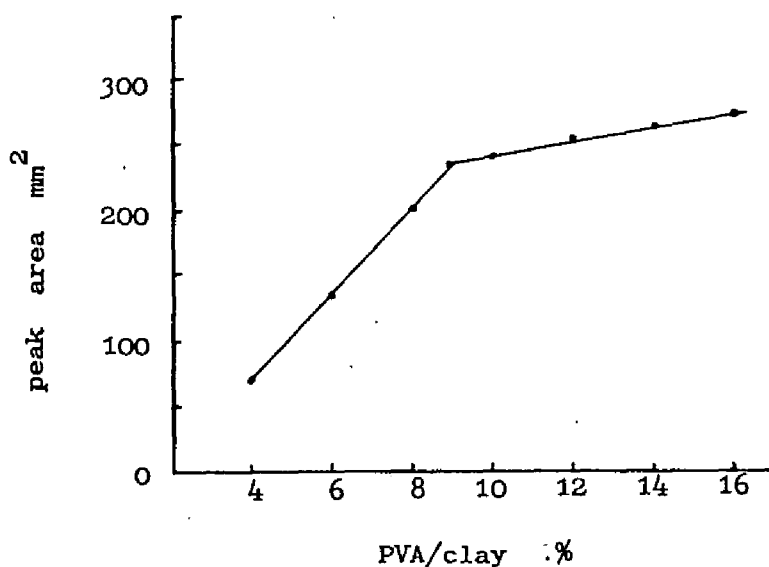


Figure 6.19 Relationship between peak area and amount of PVA added

This figure shows that when about 9 % of polymer was added to the clay, the stereo hindrance of PVA-2 to adsorption is observed remarkably.

The results of PVA-4-Na-Bent complexes are presented in Figure 6.20, Table 6.11 and Figure 6.21.

Figure 6.21 shows that the stereo hindrance of PVA to adsorption is appeared at 5.00 %.

A relation of degree of polymerization of PVA and these points are tabulated in Table 6.12.

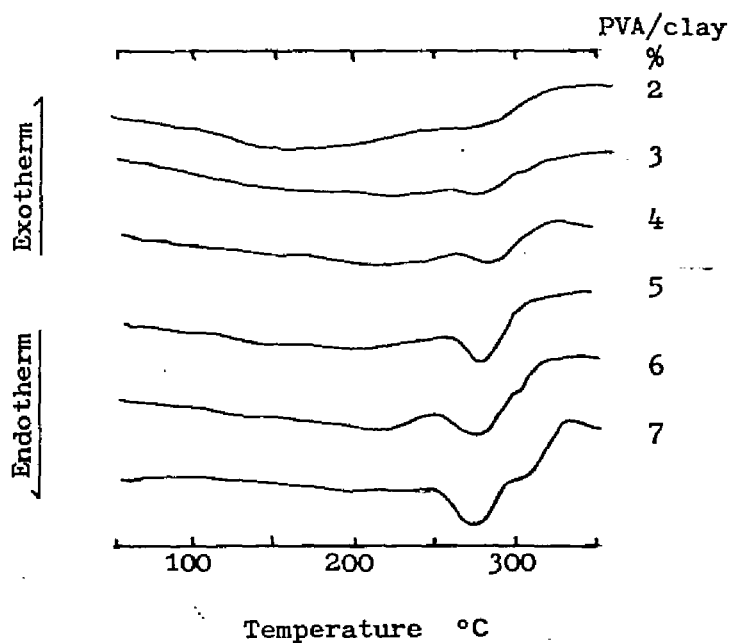


Figure 6.20 DTA curves of PVA-4-Na-Bent complex

Table 6.10 Area of endothermic peak due to PVA adsorbed
(PVA-2-Na-Bent)

PVA/clay, %	Area of endothermic peak, mm^2		mean, mm^2
	1	2	
4	70.1	67.2	68.6
6	134	124	129
8	202	197	199
9	236	231	233
10	251	234	242
12	260	256	258
14	261	267	264
16	277	267	272
20	282	282	282

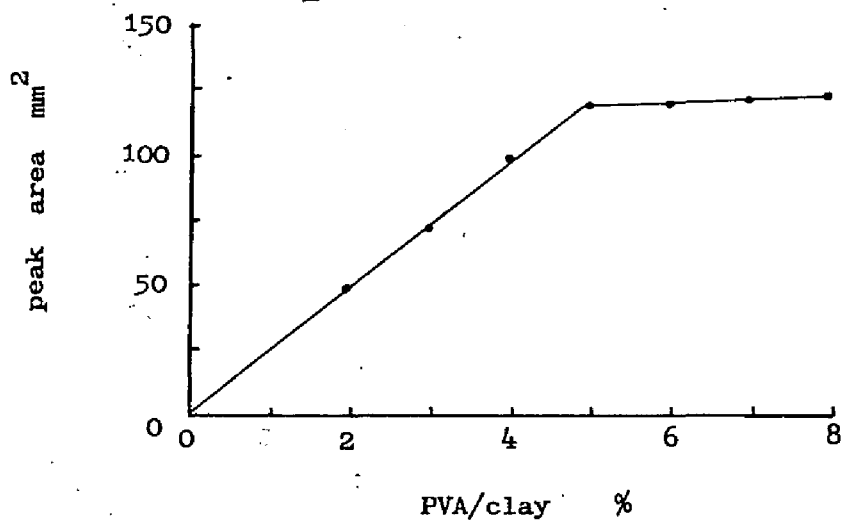


Figure 6.21 Relationship between peak area and amount of PVA added

Table 6.11 Area of endothermic peak due to PVA adsorbed
(PVA-4-Na-Bent)

PVA/clay, %	Area of endothermic peak, mm ²		mean, mm ²
	1	2	
2	51.1	45.3	48.2
3	70.1	75.9	73.0
4	104	97.8	101
5	130	120	125
6	130	133	131
7	140	142	141
8	150	146	148

ii. Discussions

The stright lines of Figure 6.17 and Figure 6.19 do not across with the intersections of two axes, while other two across with this point and slopes of the former two lines are somewhat different from those of the latter two. This reason could not be clarified in this experiment.

Relationship between the degree of polymerization (P) of PVA and point A, i.e. the ratio of PVA added to the clay at this point is presented in Table 6.12 with other relationships.

Now ratio (A) of surface area covered with PVA molecules at point A to total surface area of the clay is calculated by equation given :

$$(A) = 1820 A / 410$$

where 1820 is the area in m^2 covered by mono-layer of PVA molecule of one gram, 410 is the surface area of clay used in this experiment determined by glycerole retention method⁵⁷⁾ and A is the amount of PVA added at point A.

Values of (P), (A), log (P) and log (A) are tabulated in Table 6.12.

Relationship between log (P) and log (A) is illustrated in Figure 6.22

Table 6.12 Relations among (P), A, (A), log (P) and log (A)

(P)	A	(A)	log (P)	log (A)
300	10.35	46.0	2.477	1.663
500	9.00	39.6	2.699	1.598
1700	5.95	26.6	3.230	1.425
2700	5.00	22.2	3.431	1.346

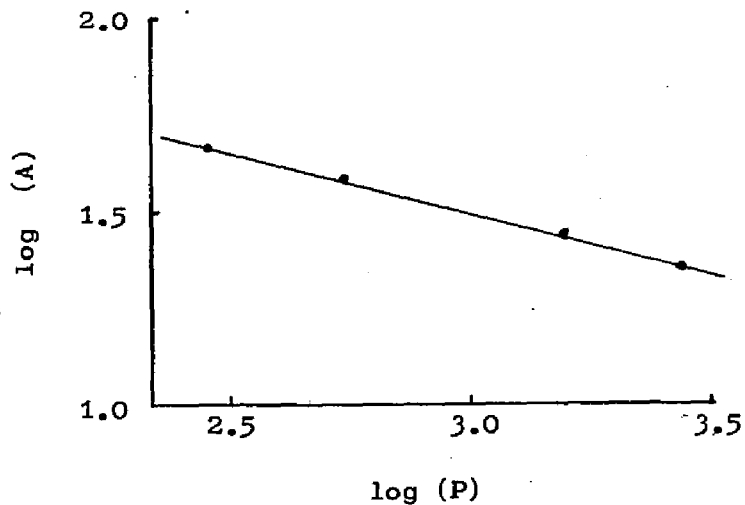


Figure 6.22 Relationship between log (P) and log (A)

As shown in Figure 6.22, log (P) and log (A) has linear relationship.

The equation of this line is presented by equation (1)

$$\log (A) = \log C_1 + \log (P) \quad (1)$$

equation (1) is represented in equation (2)

$$(A) = C_1 (P)^{-a} \quad (2)$$

Values of C_1 and a were calculated from Figure 6.22 and

$$C_1 = 316 \text{ and } a = -1/3$$

Substituting these values into equation (2), equation (3) is obtained

$$(A) = 316 (P)^{-1/3} \quad (3)$$

Now some concrete values of (P) are substituted to equation (3),

(P) = 1000		(A) = 31.6 %
(P) = 100		(A) = 68.0 %
(P) = 10		(A) = 216 %
(P) = 1		(A) = 316 %

In the case of (P) is 100 and 1000, values of (A) obtained seem to be reasonable, but other two values are unreasonable. This inconsistency is explained when we realize the characteristic behaviours of polymer molecules, namely relationship presented by equation (3) is adopted to polymer adsorbent.

A relationship between the radius of PVA molecules in its aqueous solution (R) and the degree of polymerization of PVA (P) is calculated from the results presented by Hosono et al⁴⁹⁾.

This relationship is given in equation (4)

$$(P) = C_2 (R)^2 \quad (4)$$

C_2 ; constant

From equation (2) and (4), one derives equation (5)

$$(A) = C_3 (R)^{-2/3} \quad (5)$$

$$C_3 = C_1/C_2$$

Equation (5) suggests some relationship between stereo hindrance

of polymer molecules to adsorption in the dry state.

Shimha et al.⁹²⁾ studied about the adsorption of flexible macromolecules, especially about the formation of monolayer of polymer from its dilute solution and they reported that only a fraction of $t^{-1/2}$ of the total number t of chain segments is deposited on the average and the adsorbed segments are arranged in short sequences, separated by bridges extending into the solution.

Considering from their results, relationship between the number of adsorbed point of polymer (N_1) and the degree of polymerization (P) is presented by equation (6)

$$(N_1) = C_4 (P)^{-1/2} \quad (6)$$

C_4 ; constant

Relationship between amount of PVA adsorbed when 11 % of PVA are added (A') to the clay and (P) is illustrated in Figure 6.23

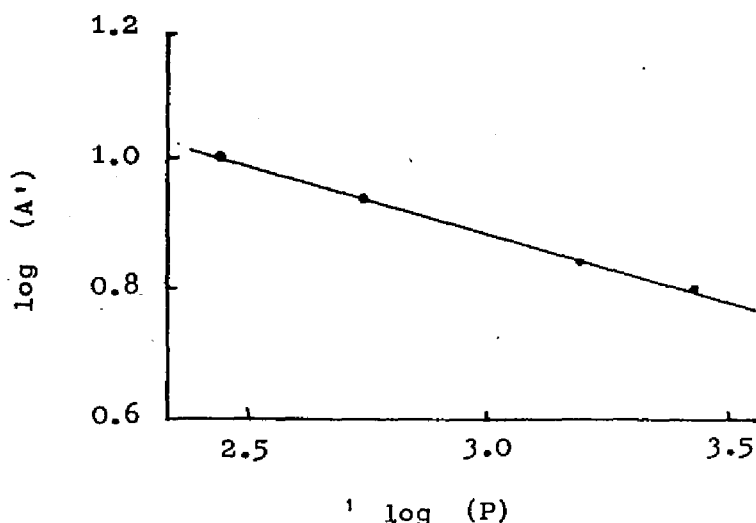


Figure 6.23 Relationship between log (P) and log (A')

The equation of this line is presented in equation (7)

$$\log (A') = \log C_5 - 1/5 \log (P) \quad (7)$$

C_5 ; constant

From equation (7), the number of adsorbed point (N_2) is presented as equation (8)

$$(N_2) = C_5 (P)^{-1/5} \quad (8)$$

From equations (6) and (8), a relation which suggests the changes in the number of adsorbed point from solution to dried state will be obtained.

$$(N_2) / (N_1) = C (P)^{0.3} \quad (9)$$

C ; constant

Equation (9) means that number of adsorbed point is increased through drying process.

6.5 Relationships between water stability of the complex and amount of polymer adsorbed on the clay surface

In Chapter 4 , the author has discussed the roles of polymer adsorbed on clay surface to water stability of PVA-Bent complexes.

Some assumptions about relation between polymer adsorbed on the clay surface and water stable characters of the complexes have been also presented.

Now a method to determine the amount of PVA adsorbed on clay surface has been devised, so using this method, relations between water stable characters of the complexes and the amount of PVA adsorbed on clay surface will be clarified in this paragraph.

i. Materials and methods

Materials

Complexes samples used were the same samples used in paragraph 2 of Chapter 4.

Methods

Determination of the amount of PVA adsorbed was conducted by using the method devised in the former paragraph in this Chapter.

Determination of amounts of PVA adsorbed on inner surface of montmorillonite.

As mentioned in Chapter 3, the peak area of X-ray diffraction diagram is nearly equivalent to the amount of materials giving that diffraction peak. Using this fact, the author intends to devise a method to separate PVA adsorbed on clay surface into two parts, i.e. PVA adsorbed on outer surface and that adsorbed on inner surface of montmorillonite.

It is assumed that the distribution of polymer molecules in a complex would be uniform when polymer and clay are reacted under the condition of existing of large amount of water. Under this assumption it is inferred that the area of X-ray diffraction peak due to the complex is corresponded to the amount of PVA adsorbed onto inner surface of montmorillonite,

Combining the area of diffraction peak and outer and inner surface of montmorillonite, one can decide the amount of PVA adsorbed on outer and inner surface of montmorillonite separately.

X-ray diffraction diagrams for the clay used, complex A and complex B are illustrated in Figure 6.24.

Here complex A was prepared under the condition of existing large amount of water during the reaction of PVA and clay, while complex B was prepared under the condition of smaller amount of water.

In the complex A, PVA molecules would be distributed uniformly on whole surface of the clay.

Comparing diagrams in Figure 6.24, it is known that the peak due to montmorillonite in which PVA molecules are adsorbed on inner surface is appeared at 4.5° in 2θ , while original montmorillonite

shows the peak at 7° to 9° in 2θ .

In these diagrams, P_c shows the peak due to montmorillonite in which PVA molecules are adsorbed on inner surface and P_c' shows the same complex, P_m shows the peak due to the original montmorillonite.

On the other hand, the amount of PVA adsorbed onto the clay surface in complex A was determined by the DTA method to be A_t grams per 100 grams of the clay. The amount of PVA adsorbed onto inner surface of the clay A_i in this complex is determined from the equation (1)

$$A_i = 340 A_t / 410 \quad (1)$$

where 340 and 410 are the areas of inner and total surface of the clay used in m^2 per gram of clay, respectively.

A relationship between A_i and P_c is presented in equation (2)

$$A_i = k \bar{P}_c \quad (2)$$

where $\bar{P}_c$ presents the area of peak P_c and k shows proportional constant.

Using the relationship of equations (1) and (2), the amount of PVA adsorbed onto inner surface of the clay in the complex B is decided as follow;

$$A_i' = \bar{P}_c' A_i / \bar{P}_c \quad (3)$$

where $\bar{P}_c'$ is the area of peak P_c' .

Of course the amount of PVA adsorbed on outer surface of the clay A_o and A_o' are calculated by equations (4) and (5), respectively.

$$A_o = A_t - A_i \quad (4)$$

$$A_o' = A_t' - A_i' \quad (5)$$

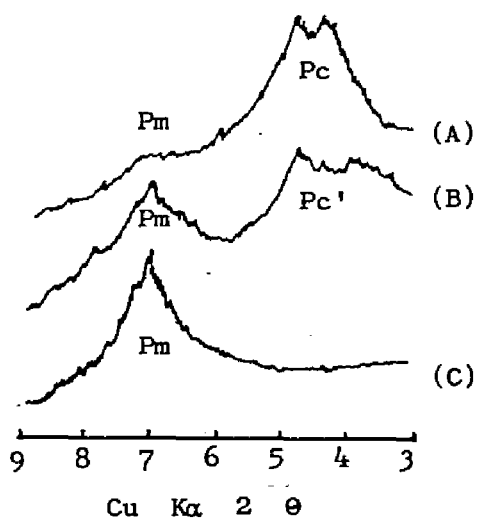


Figure 6.24 X-ray diffraction patterns of complexes A, B and clay used (C).

ii. Results and discussions

Results

DTA curves and X-ray diffraction diagrams for the complex in which 6 % of PVA was added are illustrated in Figures 6.25 and 6.26, respectively.

Area of the endothermic peak due to PVA adsorbed on clay surface is given in Table 6.13.

From these data, the amount of PVA adsorbed on outer and inner surface of montmorillonite and in free state in complexes are tabulated in Table 6.14.

Figure 6.27 presents DTA curves of the complexes in which 8 % of PVA is involved and Figure 6.28 shows X-ray diffraction diagrams for these complexes.

Results of measurement of peak area of endothermic peak due to

PVA adsorbed on clay surface and the distribution of PVA in complexes are tabulated in Tables 6.15 and 6.16, respectively.

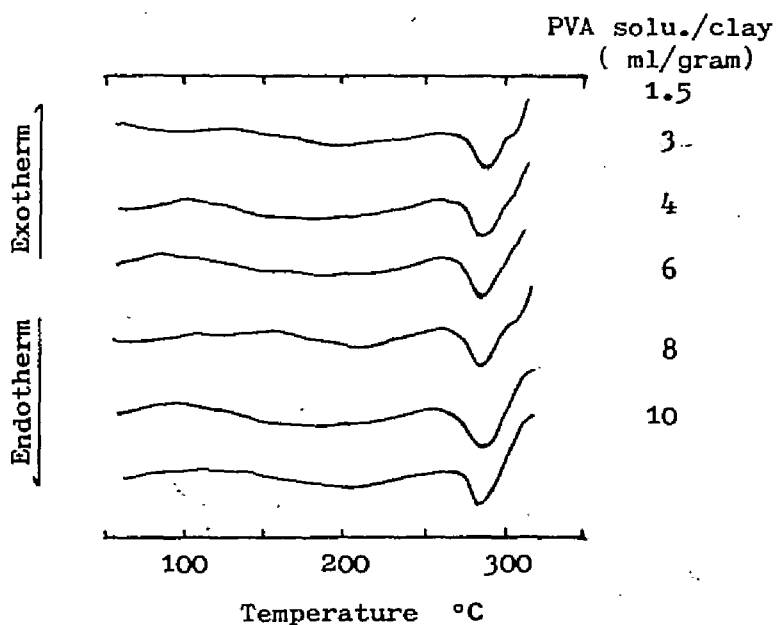


Figure 6.25 DTA curves of complex involving 6 % of PVA

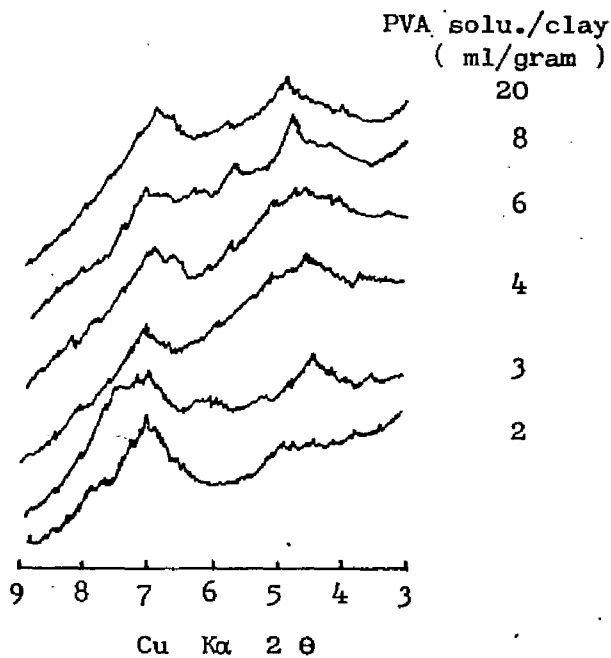


Figure 6.26 X-ray diffraction diagrams of complex (PVA:6%)

Table 6.13 Area of endothermic peak due to PVA adsorbed

PVA solu./clay (ml/gram).	Area of endothermic peak (mm ²)		mean ₂ (mm ²)
	1	2	
1.5	100	97	98.5
2	125	127	126
3	149	149	149
4	150	147	148.
6	148	147	148
8	144	144	144
10	147	147	147
20	148	147	148

Table 6.14 Distribution of PVA in complexes (PVA/clay ; 6 %)

PVA solu./clay (ml/gram)	Distribution of PVA in complex, (%)		
	inner surface	outer surface	free
1.5	28.3	36.7	35.0
2	36.9	46.7	16.4
3	49.7	49.5	0.8
4	59.0	38.3	2.7
6	64.0	33.1	2.9
8	74.3	21.5	4.2
10	68.5	29.0	2.5
20	80.8	16.7	2.5

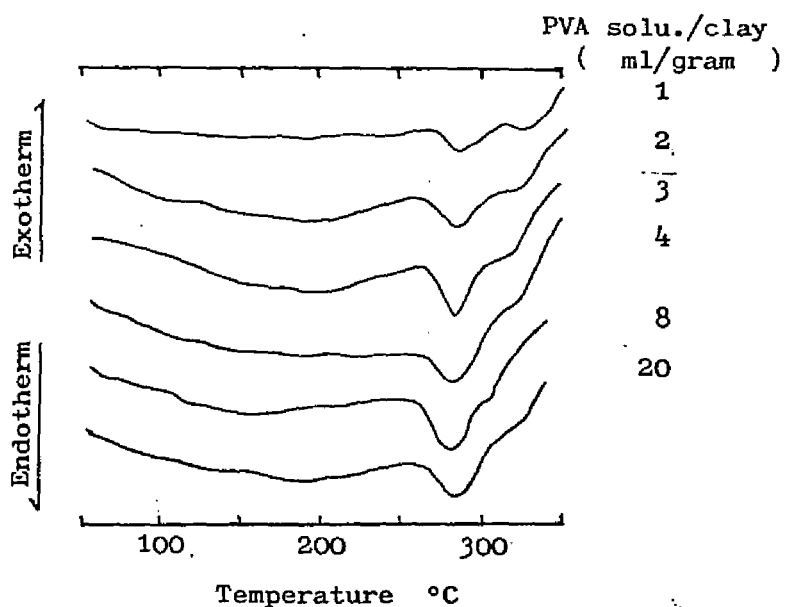


Figure 6.27 DTA curves of complex involving 8 % of PVA

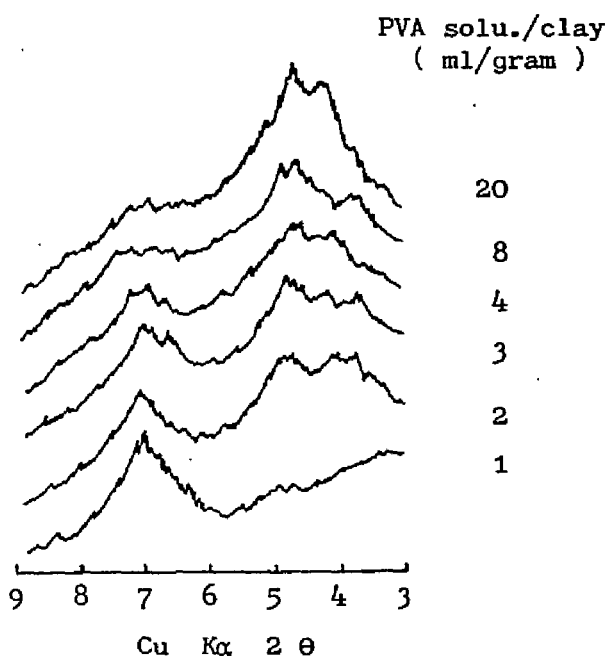


Figure 6.28 X-ray diffraction patterns of complex (PVA:8%)

Table 6.15 Peak area of endothermic peak due to PVA adsorbed

PVA solu./clay (ml/gram)	Area of endothermic peak (mm ²)			mean (mm ²)
	1	2	3	
1	83.5	83.5	87.5	84.8
2	132	132	133	132
3	156	159	163	159
4	158	157	164	159
6	158	161	155	158
8	156	160	163	160

Table 6.16 Distribution of PVA in complexes

PVA solu./clay (ml/gram)	Distribution of PVA in complex, (%)		
	inner surface	outer surface	free
1	9.75	36.5	53.75
2	30.75	34.88	34.37
3	42.88	37.12	20.00
4	49.13	30.88	20.00
8	52.90	27.10	20.00
20	66.90	13.80	19.30

Discussions

Relationship between the amount of water stable aggregate and the concentration of suspension during the reaction of PVA and clay is presented in Figure 6.29, which is the same figure with Figure 4.3. The distribution of PVA in complexes are shown in Figures 6.30 and 6.31.

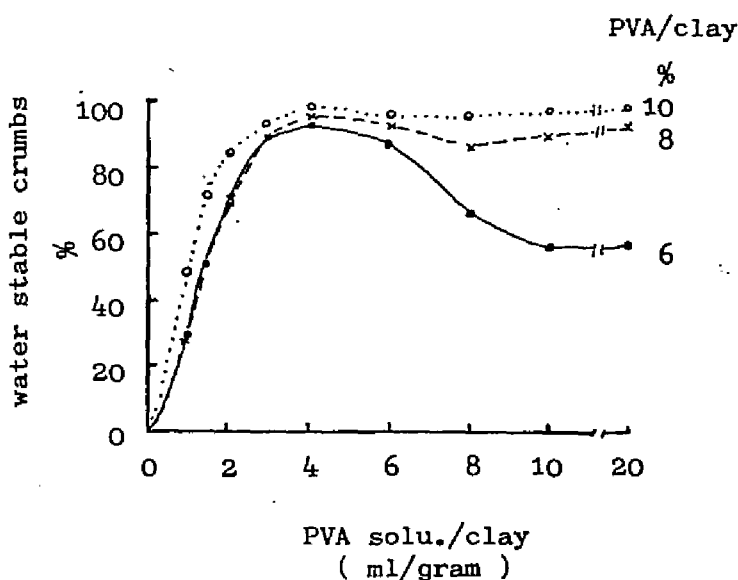


Figure 6.29 Water stability of complex and amount of PVA added

Curves in Figure 6.29 show that complexes formed under the conditions of clay suspension of 33.3, 25.0 and 16.7 % have higher water stable characters than other complexes.

Figures 6.30 and 6.31 present the answers for this higher water stability, i.e. PVA adsorbed on outer surface of the clay plays an important role for water stability of the complex. Of course PVA adsorbed on inner surface plays also important roles for this character.

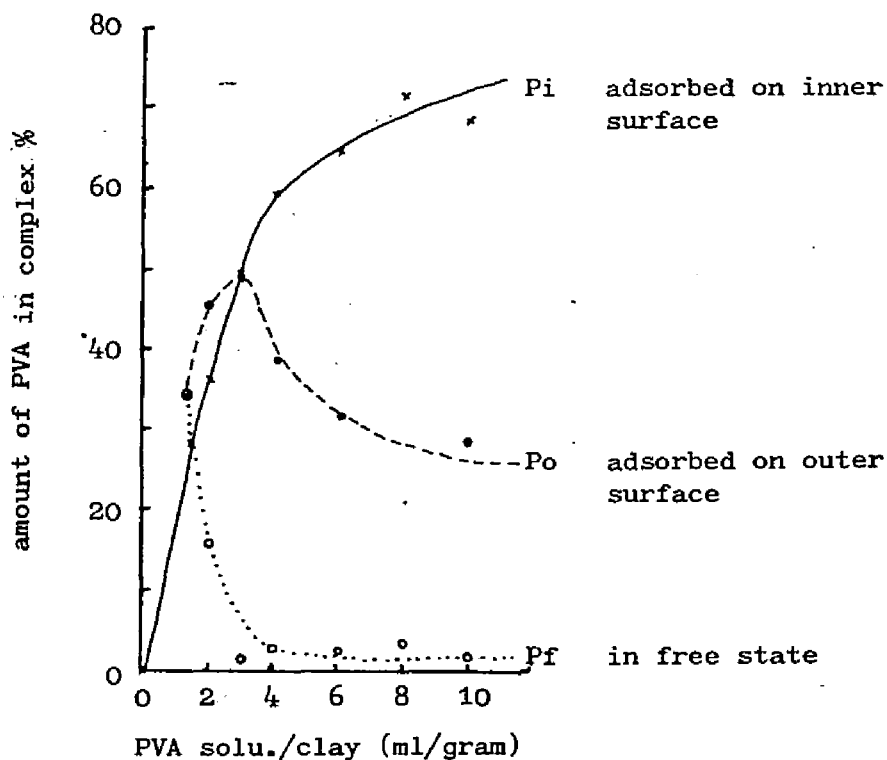


Figure 6.30 Distribution of PVA in complex (6%)

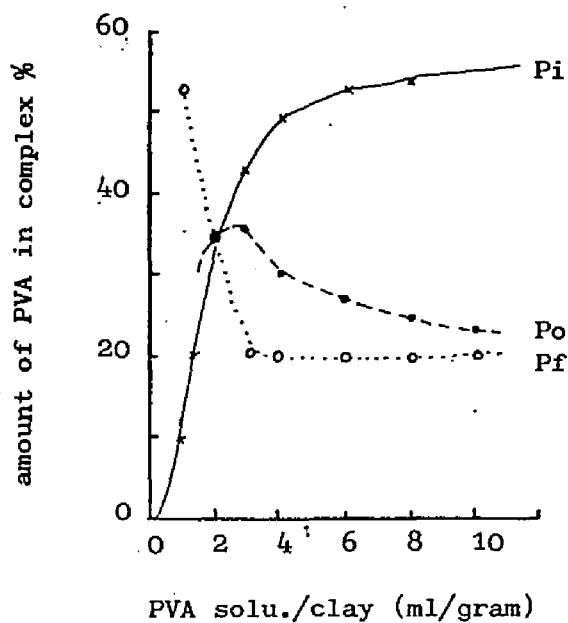


Figure 6.31 Distribution of PVA in complex (8%)

When a piece of aggregate is put into water, force acting for breaking down of the aggregate inferred to be as follow; 1) hydration of exchangeable cations of the clay, 2) formation of electric double layers through the adsorption of water molecules onto vacant surface of the clay and 3) the repulsive force acting between two electric double layers. Among these forces, the formation of electric double layers seems to play main role for breaking down of the aggregate.

On the other hand, force acting against above mentioned force is supposed to be as follow; 1) PVA molecules adsorbed onto inner surface of the clay which act for restricting the hydration of inner surface and for bonding of adjacent two layers, 2) PVA molecules adsorbed onto outer surface of the clay which act for hindrance to hydration of outer surface of clay and for formation of interparticles bridges.

Here it is inferred that PVA adsorbed on outer surface of the clay would restrict the dispersion of water molecules into inner surface of the clay, so PVA molecules of this part would play main role in counteracting to breaking force.

Relations between water stability of PVA-Bent complexes and the amount of PVA adsorbed on clay are illustrated in Figure 6.32.

These complexes in Figure 6.32 are divided into four groups according to their water stable characters.

Difference of adsorption place dose not appear as difference of water stabilities of complexes in groups A and D. While in groups B and C, in which about the same amount of PVA are adsorbed, the difference of adsorption place of PVA molecules appears as the difference in water stabilities of complexes, The amount of PVA adsorbed on outer surface of clay in the complexes of group C is larger than that of group B.

Here the role of PVA molecules adsorbed on outer surface of clay is clarified in relation to water stability of complex.

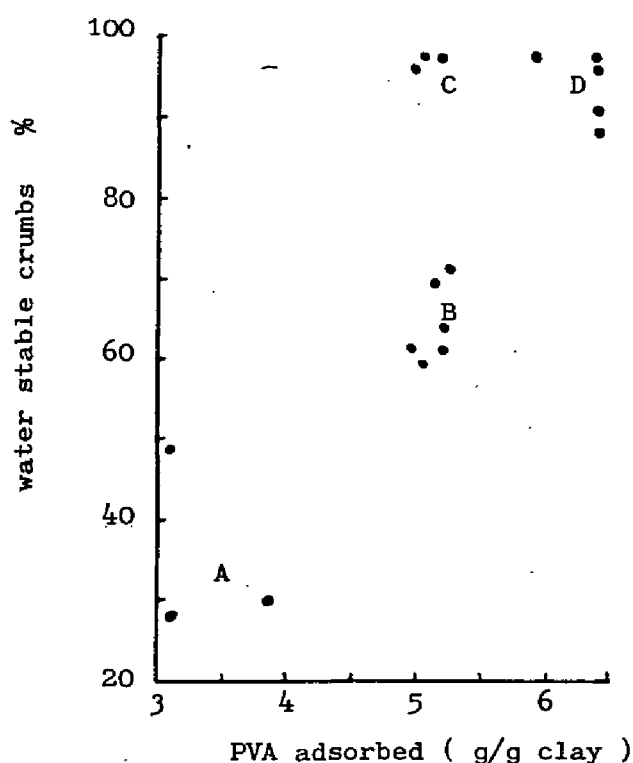


Figure 6.32 Relationship between water stability of complex and amount of PVA adsorbed.

6.6 Summary

Results obtained in this Chapter are summarized as follow;

Using DTA technique, PVA molecules in PVA-Bent complexes were separatively analysed according to their existing states.

A relationship between the degree of polymerization of PVA and stereo hindrance of polymer to adsorption was studied and was got following relationship between the degree of polymerization of PVA (P) and the amount of PVA added when the hindrance begins to appear remarkably A.

$$A = C \cdot (P)^{-1/3} \quad C ; \text{constant}$$

Change in number of adsorbed points from solution (N_1) to dry state (N_2) in PVA-Bent complex is presented as a relationship of equation

$$(N_2) / (N_1) = C (P)^{0.3} \quad C; \text{ constant}$$

PVA molecules adsorbed on outer surface of montmorillonite play an important role on water stability of complex of PVA and Na-Bent, though those adsorbed on inner surface play also important roles on this property of complex.

CHAPTER 7

A PROPOSAL OF NEW METHOD FOR THE DETERMINATION OF AMOUNT OF ADSORBED POLYMER TO CLAY PARTICLES FROM SOLUTION

The adsorption of polymer from solution onto a solid surface differs from that of small molecules in several respects.

1) Most polymer molecules are flexible to some degree and possess many internal degrees of freedom. Some of which are lost or restricted when adsorption takes place. The extent to which the intermolecular configurations of the polymer molecules are limited is an important factor in the analysis of polymer adsorption.

2) By virtue of its great mass, a polymer molecule diffuses very slowly and further, because of its size and low mobility it does not penetrate into pores on solid surface which are easily accessible to smaller molecules. As a result, geometric irregularities on an absorbent surface.

3) The polymer consists of repeated identical chemical groups along the molecules, any one or all of which may be bound to the absorbent surface in contrast to smaller molecules which are adsorbed at a single absorbent site.

In the suspension system of polymer-absorbent particles-medium, one can observe the results of polymer adsorption onto particles as phenomena of flocculation and deflocculation of the particles in the system or phenomena of changes in rheological behaviors of the system, which are important in industrial standpoints.

In the studies of adsorption, it is very important to get adsorption isotherms to clarify those phenomena.

The first step of getting the adsorption isotherms is to determine the amount of adsorbed matters, so many methods have been devised to determine the amount of adsorbed polymer onto solid surface.

The theoretical grounds of those methods are divided into three categories 8), 31), 63), 67), 94).

1) is to know the weight change of absorbent in polymer solution by particular balance.

2) is chromatgraphic measurement.

3) is so to speak the centrifugal method.

Only the method of theory 3) has been employed for the system of polymer-powder absorbent-medium and those of 1) and 2) have no efficiencies for that system.

So the centrifugal method will be explained into some details.

In this method the absorbent is added to polymer solution of known concentration then after adsorption equilibrium is attained, the concentration of supernatant solution is decided. The difference of concentration of polymer solution before and after adsorption gives the amount of adsorbed polymer.

The centrifugal method consists of three processes.

First process is the reaction of absorbent and polymer.

Second process is to separate clear supernatant solution from the system.

Third process is to analyse the polymer concentration of the supernatant solution then calculate the amount of adsorbed polymer onto absorbent.

Development of this method seems to have been made by two factors, i.e. progression of centrifugal technique and analytical method. The former makes it possible to separate clear supernatant solution from any suspension and the latter makes it possible to determine the concentration of supernatant solution.

Almost all works reported have employed the centrifugal method.

But there are important problems in the second process of this method, i.e. centrifugal process. It is wondered whether centrifugal process may disturb the adsorbed polymer layers and moreover whether the non-adsorbed polymer may be precipitated in the process of pre-

cipitating of absorbent particles.

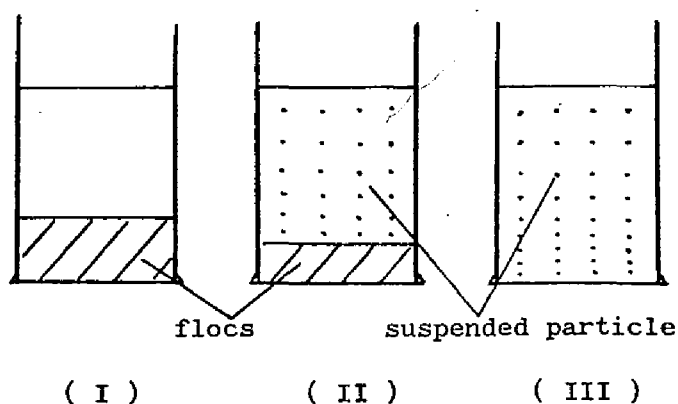
The author intends to examine this centrifugal method by devising new method. The new method was devised by using the characteristic behaviours of the system of polymer-clay-water.

The theoretical ground (7.1) and the results of the experimental test for this method applied to PVA-Na-Mont-Water sytem and the comparisions of the results of this method and those of the centrifugal method will be presented in Paragraph 7.2.

7.1. Theory

The system of polymer-clay-water shows various phenomena of flocculation -deflocculation at the adsorption equilibrium.

Those phenomena are classified into three types shown in Scheme 7.1.



Scheme 7.1 Typical phenomena of polymer-clay-water systems

where Type 1 ; All absorbent particles are flocculated and clear supernatant solution is separated naturally.

Type 2 ; A part of absorbent particles is flocculated to precipitate and other parts of them are suspended in the medium (polymer solution).

Type 3 ; For our naked eyes, the system of this type appears a homogeneous suspension of absorbent particles.

More detail observation on the system in Type 3 shows this type is the same with that of Type 2, so it is concluded that only Type 2 is the typical mode of flocculation-deflocculation of polymer-clay-water system.

The theory will be derived from the system in Type 2.

As shown in Figure 7.2, two samples A and A' are pipetted out from the system in adsorption equilibrium, then depth of sampling is different. Samples taken out involve four factors shown in equations (1) and (2).

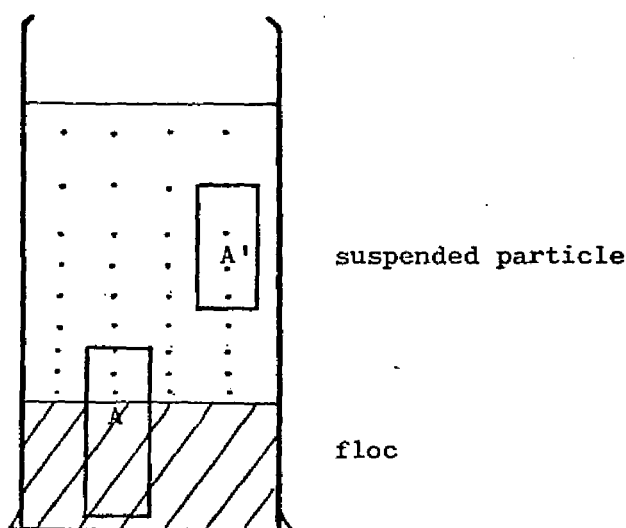


Figure 7.2 Method of sampling

$$A = a + b + c + d \quad (1)$$

$$A' = a' + b' + c' + d' \quad (2)$$

where A (A') is weight of sample A (A'), a (a') is weight of absorbent in A (A'), b (b') is weight of polymer adsorbed on absorbent in A (A'), c (c') is weight of polymer in free state in A (A') and d (d') is weight of medium in A (A').

In the state of adsorption equilibrium of the system, assume that the ratio of weight of adsorbed polymer onto definite mass of absorbent is uniform throughout the system and the polymer concentration of medium is also uniform throughout the system. These two assumptions are presented in equations (3) and (4).

$$b/a = b'/a' \quad (3)$$

$$c/d = c'/d' \quad (4)$$

Drying these samples one gets B and B' shown in equations (5) and (6).

$$B = a + b + c \quad (5)$$

$$B' = a' + b' + c' \quad (6)$$

Weight of polymer in samples are presented in equations (7) and (8).

$$C = b + c \quad (7)$$

$$C' = b' + c' \quad (8)$$

Dividing equations (7) and (8) by d and d' , respectively, one gets equations (9) and (10)

$$\frac{C}{d} = \frac{b}{d} + \frac{c}{d} \quad (9)$$

$$\frac{C'}{d'} = \frac{b'}{d'} + \frac{c'}{d'} \quad (10)$$

Subtracting equation (10) from equation (9)

$$\frac{C}{d} - \frac{C'}{d'} = \left(\frac{b}{d} - \frac{b'}{d'} \right) + \left(\frac{c}{d} - \frac{c'}{d'} \right) \quad (11)$$

the second term of right hand side of equation (11) is zero owing to the relationship of equation (4) so equation (11) becomes

$$\frac{C}{d} - \frac{C'}{d'} = \frac{b}{d} - \frac{b'}{d'} \quad (12)$$

eliminate b' from equations (3) and (12) and rearrange the obtained equation, one gets b

$$b = \left(\frac{d'C - dC'}{dd'} \right) \cdot \left(\frac{add'}{ad' - a'd} \right) \quad (13)$$

so ratio of weight of polymer adsorbed to that of absorbent is given by equation (14)

$$\frac{b}{a} = \frac{d'C - dC'}{ad' - a'd} \quad (14)$$

and concentration of polymer solution is also given by equation (15)

$$\frac{c}{d} = \frac{aC' - a'C}{ad' - a'd} \quad (15)$$

All factors in equations (14) and (15) can be obtained by experiment.

So it is concluded that the amount of polymer adsorbed onto absorbent particles could be calculated by using the relationships of equations of (14) and (15), if the assumptions of equations (3) and (4) are correct.

Here it is necessary to examine the validity of two assumptions through experiment.

7.2. Materials and methods

Materials

Clay used in this experiment is Na-Mont and polymer used is PVA 3'.

Methods

Na-Mont suspension was mixed with PVA 3' solution in a vessel, the final concentration of clay suspension was adjusted to be 0.5 %, then this system was mixed. Reacting time employed was 48 hours and at the end of this time interval samples for analysis were pipetted out.

Factors needed for calculation were determined by following methods;

B : weight of sample after drying for 24 hours at 110 °C.

C : Determination of polymer weight of sample was made by oxidation of polymer with excess standard dicromate/sulfuric acid mixtures and determination of the excess dicromate with standard ferrous ion solutions. The volume of dicromate required to oxidize a given amount of polymer was determined using standard solution of the polymer and montmorillonite suspension. Oxidation was conducted

under the conditions of 180 ± 3 °C. for 10 minutes. Under this condition high reproducibility of calibration curves were gained.

The amount of polymer in the samples could be determined within ± 0.05 mg.

a : Weight of clay in the samples was obtained by subtracting C from B.

d : Weight of solvent was calculated by equation of $(A - B)$.

Of course the values of B', C', a' and d' were determined the same ways employed above.

Comparison with centrifugal method

To compare with centrifugal method, samples were centrifuged under the gravitation of 16,000 g. for 30 minutes and supernatant solution obtained was analysed by the oxidation method presented above, and the amount of polymer adsorbed was determined from the change in concentration of polymer solution before and after adsorption.

All experiments were carried out by duplication and amount of polymer adsorbed were expressed by grams of polymer per gram of clay dried at 110 °C.

7.3. Results and discussions

To examine the validity of the assumptions employed for the derivation of the new method, three samples were pipetted out from different depth of a system. From these samples, one can obtain three values of b/a . If those three values coincide each other, the validity of the assumption would be certified.

Results of analyses are tabulated in Tables 7.1, 7.2, 7.3 and 7.4.

Amounts of adsorbed polymer calculated from these four tables are tabulated in Table 7.5.

Results of the centrifugal method for the same samples are shown in Table 7.6.

Table 7.1 Results of analysis of System 1
(PVA/Mont : 19.62 %)

	A	B	D	(grams) a	d
I	9.99810	0.13005	0.02144	0.10861	9.86805
	A'	B'	D'	a'	d'
II	12.45240	0.05600	0.00955	0.04645	12.39640

Table 7.2 Results of analysis of System 2
(PVA/Mont : 29.42 %)

	A	B	D	(grams) a	d
I	9.98155	0.15680	0.03491	0.12189	9.82475
	A'	B'	D'	a'	d'
II	12.45300	0.05465	0.01261	0.04204	12.89835
	A''	B''	D''	a''	d''
III	14.88560	0.09935	0.02232	0.07703	14.78625

Table 7.3 Results of analysis of System 3

(PVA/Mont : 39.24 %)

	A	B	D	(grams) a	d
I	9.98235	0.15990	0.04250	0.11740	9.82245
	A'	B'	D'	a'	d'
II	12.44145	0.06485	0.01865	0.04620	12.37600

Table 7.4 Results of analysis of System 4

(PVA/Mont : 49.04 %)

	A	B	D	(grams) a	d
I	10.00150	0.21115	0.06116	0.14999	9.79035
	A'	B'	D'	a'	d'
II	12.43790	0.06220	0.02217	0.04003	12.37570
	A''	B''	D''	a''	d''
III	14.84210	0.09880	0.03322	0.06558	14.74330

Table 7.5 Amounts of polymer adsorbed

System	Amount of PVA adsorbed on clay (grams/gram clay)	prob. error
1	0.193	
2	mean value 0.279	0.003
3	0.343	
4	mean value 0.372	0.004

Table 7.6 Results of the centrifugal method

	System			
	1	2	3	4
Conc. of supernatant (%)	0.0010	0.0011	0.0123	0.0290
Amount of PVA adsorbed (grams/gram clay)	0.194	0.292	0.367	0.433

Discussions

Validity of the assumptions and this new method

Validity of this new method will be examined from the results of Tables 7.2 and 7.4.

Probable error of mean values are 0.003 and 0.004 for results Tables 7.2 and 7.4, respectively. These small probable errors show that the assumption used in derivation of the theory was correct and this method also correct to determine the amount of adsorbed polymer from solutions to powder absorbent.

Comparison of this new method with the centrifugal one

Now a new method of determination of the amount of polymer adsorbed is established, so using this new method as the standard the results of the centrifugal method will be checked.

In Table 7.7, results of this method and those of centrifugal one are presented.

Table 7.7 Comparison of the results of this new method with those of the centrifugal one

		System			
		1	2	3	4
Amount of PVA adsorbed on clay (g/g clay)	centri. method	0.194	0.292	0.367	0.433
	new method	0.193	0.279	0.343	0.372
	d	0.001	0.013	0.024	0.061

where $d = \left(\begin{array}{l} \text{amount of polymer adsorbed by this method} \\ \text{amount of polymer adsorbed by the centrifugal one} \end{array} \right) -$

Data of Table 7.7 show that d value of each samples is all positive and the larger the amount of polymer added to the clay, the larger d value becomes.

This fact is explained without any inconsistency when we realize that polymer molecules in free state are precipitated in the process of precipitating of absorbent-polymer flocs in the centrifuging process.

Here one of problems involved in the centrifugal method is clarified by this new method.

7.4 Summary

Using the characteristic behaviours of the system of polymer-clay-water, a new method for determination of the amount of polymer adsorbed onto clay has been devised.

Usually for the above mentioned system, the determination of the amount of polymer adsorbed has been conducted by the analysis of the polymer solution before and after adsorption, and always a centrifugal process has been employed to gain clear supernatant solution which is offered to the analysis of polymer concentration after adsorption.

But this routine centrifugal method has problems which derive wrong results about the amount of polymer adsorbed.

This fact is certified by this new method.

CHAPTER 8

MECHANISMS OF BONDING BETWEEN POLYVINYL ALCOHOL AND MONTMORILLONITE

A few works concerning with the mechanisms of bonding between polyvinyl alcohol and montmorillonite have been reported.

Emerson¹⁸⁾ once reported that the bonding mechanism is van der Waals' force between them, but later he altered this to be hydrogen bonding between them¹⁹⁾.

From X-ray diffraction analysis data and the properties of PVA monomolecular layer adsorbed onto the clay, the author certified this mechanism to be hydrogen bonding between OH groups of PVA molecules and Oxygen atoms of silica-tetrahedral layer of montmorillonite.⁸⁰⁾

Kita⁶⁰⁾ also reported this to be hydrogen bonding between them from his X-ray data.

In these works the principal method employed was X-ray analysis. But as mentioned in Chapter 2, the results about interactions between organic molecules and clay derived from X-Ray data involves some degree of speculations.

For example, the result obtained by the author is shown in Figure 8.1.

The basal spacing of the complex in which two molecular layers of PVA are adsorbed onto intercrystalline lattice of montmorillonite was observed to be 17.5 to 18.3 Å when hydrogen bonding is formed between them and 20.1 Å when two molecular layers of PVA are packed between them only through van der Waals' force.

From these data it was decided that the formation of hydrogen bonding between them is more probable, but the probability of the existance of bonding through van der Waals' force did not be denied completely.

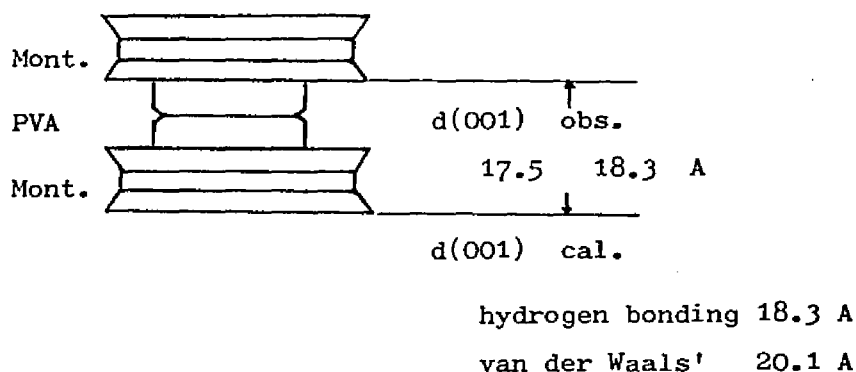


Figure 8.1 X-ray analysis of PVA-Mont. complex

Unfortunately not enough work has been done on this problem to allow any unequivocal interpretation of it.

It has been well known that one of the direct methods of studying the interactions between organic molecules and clay is infrared spectrum absorption technique, but there is no work on PVA-montmorillonite system reported which was done by using infrared technique.

In applying this technique for the studying the mechanism of bonding between PVA and montmorillonite, there were problems which would bring troublesome for the analysis of experimental data obtained.

The principal problem was how to distinguish the hydrogen bonding of inter-molecules of PVA to the hydrogen bonding between PVA and montmorillonite.

The author intends to solve this problem by employing means of combination of infrared adsorption technique with deuteration exchange.

8.1 Materials and methods

Materials

Clay sample used was Na-Mont.

Polymer samples used were PVA-1' and PVA-3'

Methods

Preparation of sample

A definite amount of PVA solution was reacted with definite volume of clay suspension in a test tube for 48 hours at room temperature, then 1 ml of suspension of PVA-clay complex was pipetted out and dropped carefully on the film of polyethylene, then dried at 50 °C. Thus airdried film of the complex was mounted on a special paper window, then this mounted sample was dried under high vacuum for 24 hours at 110 °C.

Spectroscopic measurement

Infrared spectra of samples prepared under above condition were measured by Shimadzu-model AR-27 spectrometer with NaCl prism and Hitachi-model EP 1G grating spectrometer.

Deuteration of the complex

The deuteration of one of the film samples was carried out in the deuteration cell designed by Taniguchi et al.

After mounted on the cell, the film sample was completely dehydrated by nitrogen gas dried by passed firstly through concentrated sulfuric acid and then over phosphorous pentoxide. After the dehydration of the sample the cell was fixed to the Hitachi spectrometer in order to measure the infrared spectrum of the dried sample. Then nitrogen gas was changed with D₂O vapor by let pass through deuterium oxide and then was led into the cell.

The measurement of the deutrating sample was conducted after considerable time intervals.

8.2 Results and discussions

i. Infrared spectrum absorption curves for montmorillonite mounted on the film of polyethylene and PVA film are presented in Figure 8.2.

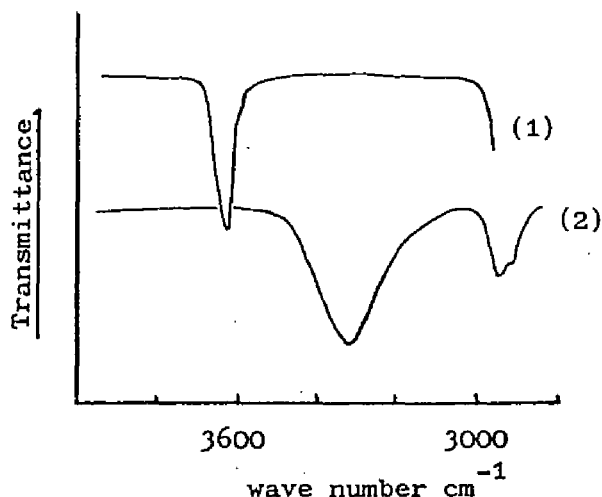


Figure 8.2 Infrared spectrum absorption curves for montmorillonite (1) and PVA (2).

where only the frequency region of 3700 to 2800 cm^{-1} is presented concerning with OH stretching vibration.

Curve 1 shows one sharp band at 3620 cm^{-1} , which depends on the stretching vibration of OH group in montmorillonite lattice and there is no other band in frequency region of 3600 to 3300 cm^{-1} . This curve shows that adsorption of water molecules onto clay surface did not occur under this experimental condition. This is very important to analyse other curves obtained from PVA-Mont complexes.

There are two bands in curve 2, one broad at 3320 cm^{-1} is due to OH stretching vibration of PVA molecules and another band at 2940 to 2900 cm^{-1} is due to the stretching vibration of CH₃ group in PVA.

In Figure 8.3, are illustrated absorption spectra of PVA-Mont

complex.

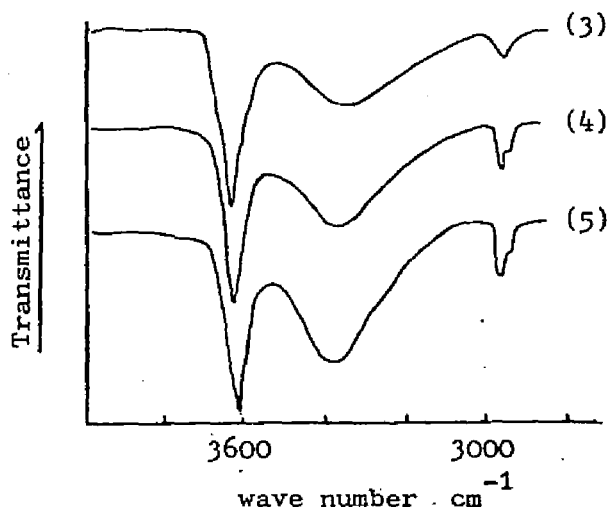


Figure 8.3 IR-spectra of PVA-Mont complex

where weight percentage of PVA added to clay for samples giving spectra 3, 4 and 5 are 6, 10 and 16 %, respectively.

As assigned above, band at 3620 cm^{-1} is due to OH group in montmorillonite lattice and band at $3320\text{ to }3340\text{ cm}^{-1}$ is due to OH...O hydrogen bonding and absorption band at $2940\text{ to }2900\text{ cm}^{-1}$ is due to CH stretching vibration..

Detail observation of these curves shows that the band of OH...O stretching vibration slides somewhat lower frequency range with increasing of PVA amount, namely the band at 3380 cm^{-1} for curve 3 slides to 3340 cm^{-1} for curve 5. In addition to this fact, band of curve 2 observed at 3320 cm^{-1} .

Results of the assignment of each bands of curves are tabulated in Table 8.1

Table 8.2 shows the values of peak intensity of each samples.

Table 8.1 Assignment of each bands in samples

Wave number, (cm^{-1})	Assignment
3620	OH stretching vibration of montmorillonite lattice
3320 3380	OH stretching vibration of hydrogen bonding
2940 2900	CH stretching vibration of PVA molecules
2500	OD stretching vibration

Table 8.2 Peak intensity of each samples

PVA/clay, %	$\log I_o/I_{CH}$	$\log I_o/I_{OH}$
2	0.0111	0.027
6	0.112	0.067
8	0.033	0.079
10	0.037	0.081
12	0.051	0.092
14	0.071	0.1367
16	0.081	0.1523
18	0.096	0.1853
20	0.0969	0.1807

ii. Infrared absorption spectrum for the deuterated PVA film is illustrated in Figure 8.4.

Intensity of absorption of spectrum by OH...O st.v. is decreased after deuteration of the sample of PVA film and a band due to OD...D st.v. appears at 2500 cm^{-1} , while OH st.v. band at 2900 cm^{-1} remains

unchanged.

Some spectra for PVA-Mont complex are presented in Figures 8.5, 8.6, 8.7 and 8.8.

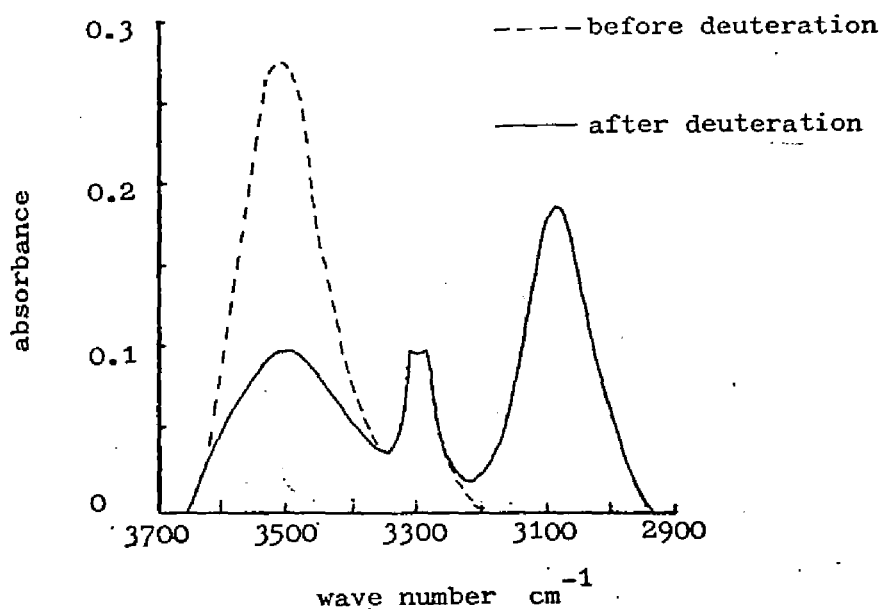


Figure 8.4 Spectrum of PVA film before deuteration (1).
after deuteration (2).

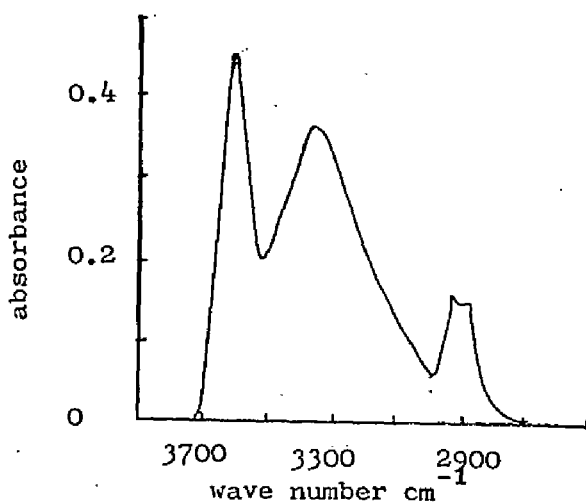


Figure 8.5 Spectrum of PVA-Mont complex dried with N_2 gas

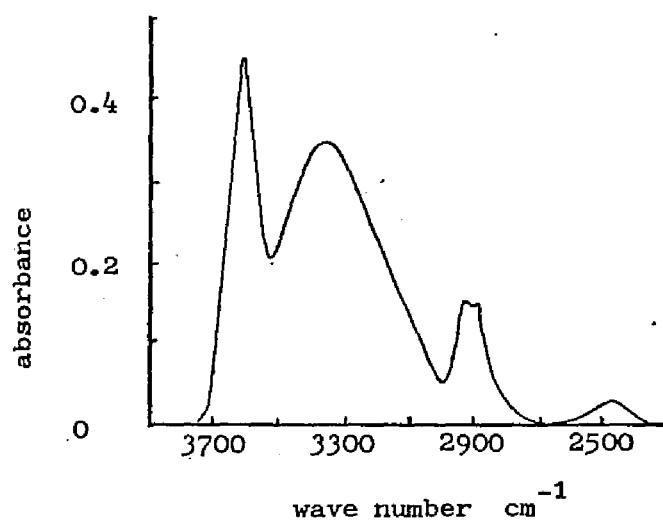


Figure 8.6 Spectrum of PVA-Mont complex deuterated for 3 hours.

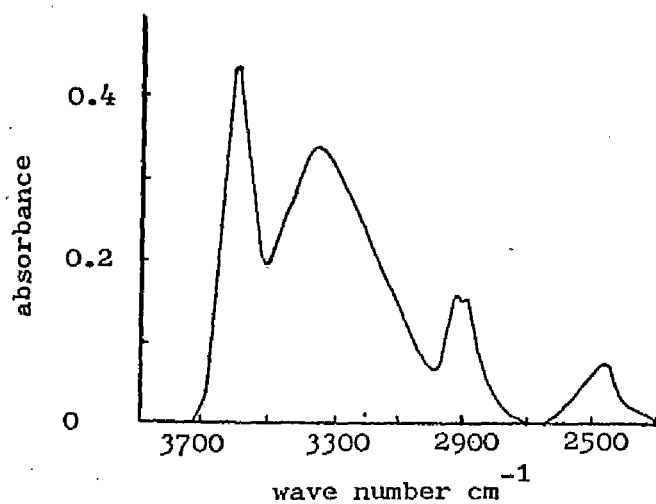


Figure 8.7 Spectrum of PVA-Mont complex deuterated for 9 hours

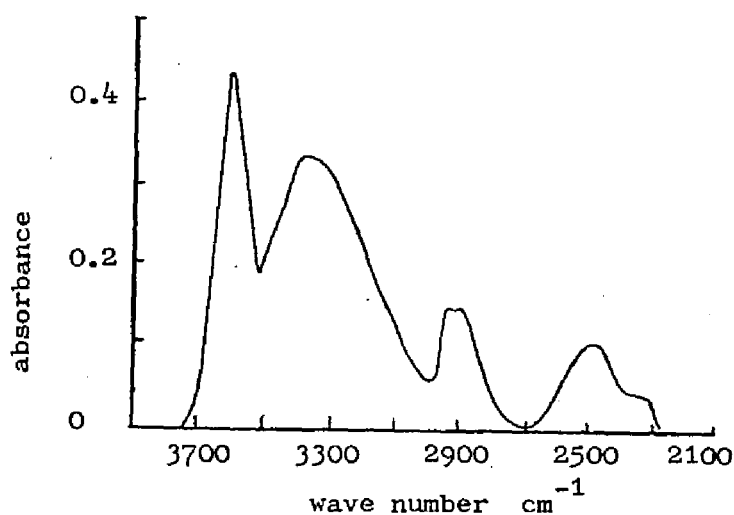


Figure 8.8 Spectrum of PVA-Mont complex deuterated for 15 hours

Results of rehydration of these samples are given in Figures 8.9 and 8.10.

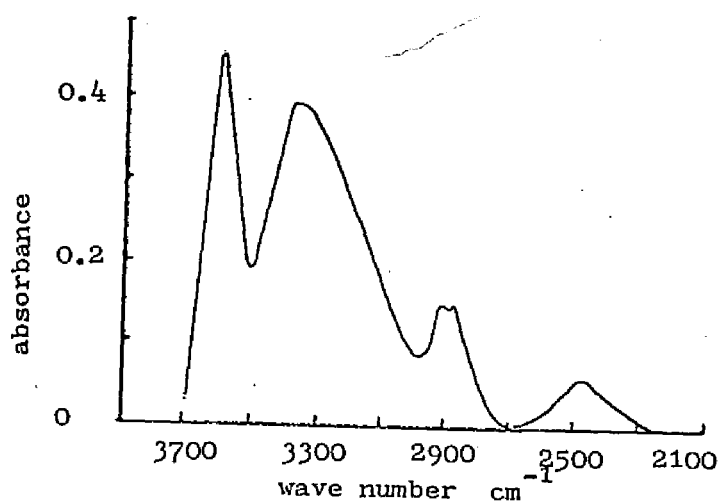


Figure 8.9 Spectrum of the complex rehydrated for 5 minutes

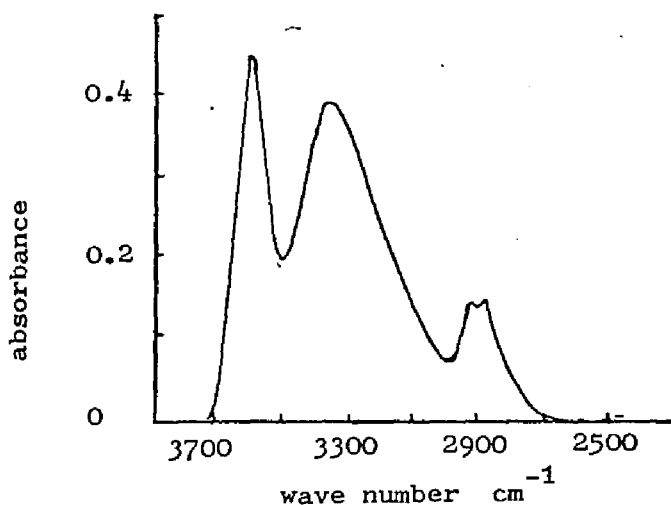


Figure 8.10 Spectrum of the complex rehydrated for 24 hours

Discussions

i. From the general characters of interaction between PVA and montmorillonite particles in suspension, behaviours of OH groups in the system are considered.

Firstly the typical flocculation-deflocculation phenomenon of the system of PVA-Mont-water is presented in Figure 8.11.

As shown in Figure 8.11, this curve is divided into three regions by the amount of PVA added. Thinking from results of Chapter 3 and 6, the behaviours of PVA molecules in each regions are thought to be as follow ;

Region A ; where all PVA molecules are adsorbed on clay surface and no formation of interparticles bonding of polymer molecules exists, so one can not observe the flocculation of the system in this region. In relation to the behaviours of OH groups in this system, it is considered that the ratio of OH in hydrogen bonding to total OH in the sytem would take a certain value. And it is also supposed that there would be no hydrogen bonding in PVA molecules in this region.

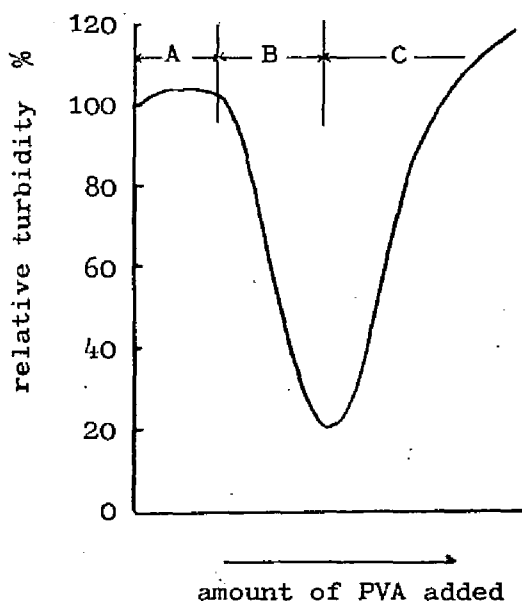


Figure 8.11 Flocculation-deflocculation of PVA-Mont system

Region B ; PVA molecules added more than region A are adsorbed on clay surface, but they also have free segments in the molecules and these free segments cause to form interparticles bonding to flocculate the system. Here again it is considered the behaviour of OH group in the system. Formation of interparticle bridges of polymer molecules suggests the existance of OH group in free state, so the ratio of OH in hydrogen bonding to total OH in the system would decrease in region B.

Region C ; where there are non-adsorbed PVA molecules, which make the system deflocculative and OH...O hydrogen bonding in PVA molecules would begin to exist and it is inferred that the further PVA added to the system, the more this type of hydrogen bonding would increase.

This consideration was examined with results of experiments.

In Table 8.3 shows ratio of absorbance of OH to that of CH₃.

Figure 8.12 shows relationship between total OH in the system and

OH in hydrogen bonding.

Table 8.3 Ratio of absorbance of OH to that of CH

PVA/clay, (%)	$\frac{\text{absorbance of OH st.v.}}{\text{absorbance of CH st.v.}}$
2	2.45
6	2.43
8	2.39
10	2.40
10'	2.37
12	1.80
12'	1.88
14	1.92
16	1.88
18	1.92
20	1.87

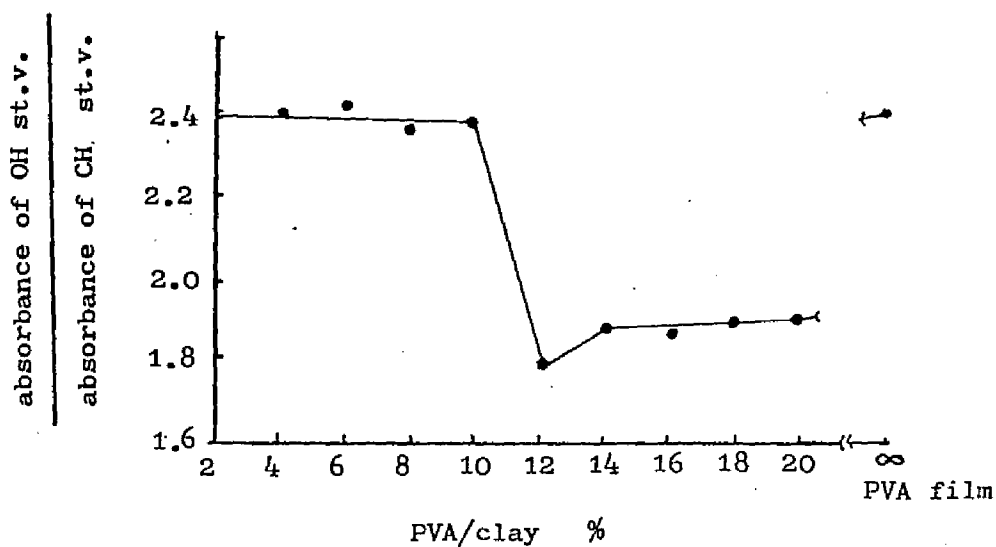


Figure 8.12 Relationship between the total OH and OH in hydrogen bonding (PVA-3')

In Figure 8.12, the ratio of absorbance due to OH...O stretching vibration to that of CH₂ stretching vibration is about 2.4 in region A and it decreases to 1.8 in region B then this value begins to increase gradually to 2.4, which is the ratio in PVA film.

It is inferred from this Figure that OH group of PVA molecules added to 10 % of montmorillonite interacts with clay surface and OH in free state begins to appear over 10 % addition of PVA, of course it is the beginning of formation of hydrogen bonding in PVA molecules.

It is concluded that OH...O hydrogen bonding in region A is due to OH in PVA molecules and oxygen atoms of silica-tetrahedral layers of montmorillonite and that OH...O hydrogen bonding due to OH groups in PVA molecules begins to appear in region B.

Here the author clarified the bonding mechanism between PVA and montmorillonite.

Another fact which supports the formation of hydrogen bonding between them is the difference in wave number of OH...O stretching vibration of PVA film and that of PVA adsorbed on clay surface. As mentioned before wave number of OH...O stretching vibration in PVA film is 3340 cm^{-1} , while that of PVA adsorbed on clay surface is $3380\text{ to }3360\text{ cm}^{-1}$. Distance of two oxygen atoms in the hydrogen bonding are 2.77, 2.83 and 2.80 Å, respectively. One of reasons which brings this difference in distance is supposed to be the difference in distribution of OH groups in PVA molecules and that of oxygen atoms in silica-tetrahedral layers of montmorillonite, namely distance of the adjacent two oxygen atoms in PVA molecules is calculated to be 2.52 Å, while that in montmorillonite surface is 2.55 Å. The difference in these two values seem to cause the difference in the distance of hydrogen bonding in two cases.

This fact becomes to be a certification of the formation of hydrogen bonding between PVA and montmorillonite.

In relation to the results of Chapter 6, stereo hindrance of PVA molecules to adsorption onto clay surface will be discussed.

The appearance of stereo hindrance is observed in region B and it is when 10 to 12 % of PVA was added to clay. This value is shifted to the higher region when smaller polymer molecule was used, which is illustrated in Figure 8.13.

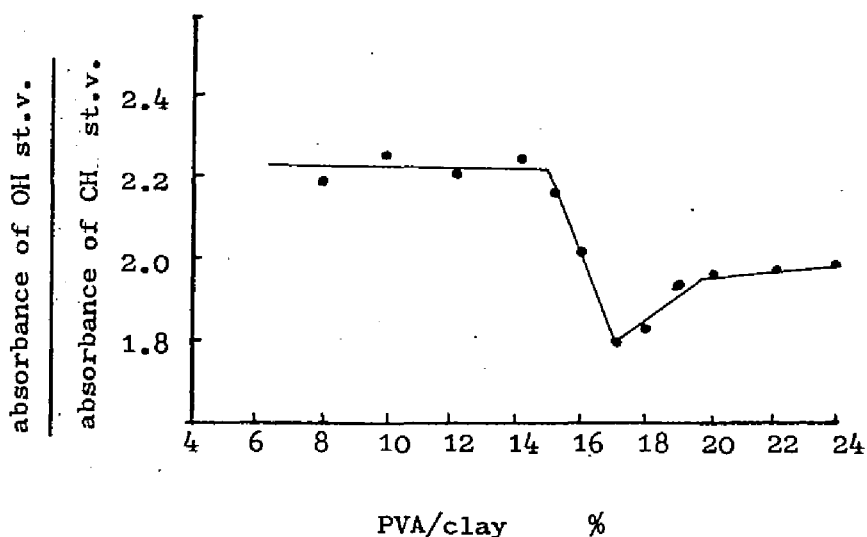


Figure 8.13 Relationship between the total OH and that in hydrogen bonding (PVA-1')

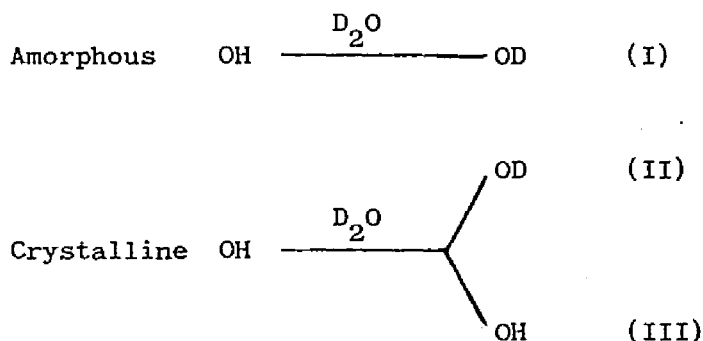
ii. The deuteration techniques have been used for studying the natures of hydrogen bonding in organic molecules. This technique has been combined with infrared analysis in investigating of hydrogen groups in organic polymers.

The author intends to utilize these techniques to studying on mechanism of bonding between PVA molecules and montmorillonite.

Results relating to this purpose are summarized as next page.

It was reported by Nitta et al. that about 90 % of OH groups in PVA film was exchanged to OD through their deuteration, but under this experimental condition only 65 % of OH groups was exchanged

to OD.



Rate of exchange (I) > (II)

From these data, following three cases are considered as the results of deuteration of the complex.

Case 1 ; PVA molecules are adsorbed on clay surface through only van der Waals' force. In this case OH groups of PVA molecules will be exchanged to OD through deuteration.

Case 2 ; OH...O hydrogen bonding are formed among PVA molecules and in this case about 65 to 90 % of OH groups will be exchanged to OD through deuteration.

Case 3 ; OH...O hydrogen bonding are formed between OH groups in PVA and oxygen atoms of clay surface, in this case there are two possibilities of exchanging process, namely one is the hydrogen bonding which has analogous character with that in PVA molecules and the other is the hydrogen bonding which is different from that in PVA molecules.

It is inferred from above data that the latter hydrogen bonding would have different character to deuteration and that the former one would have the same behaviour to deuteration.

Results of experiment given in Figures 8.5 to 8.8 show that OH...O hydrogen bonding in PVA-Mont complex is quite different from that in PVA molecules, because about 90 % of OH groups in the sample is

remained unchanged through deuteration (in Figure 8.8).

This fact suggests that about 10 to 15 % of OH groups is in the state of free or OH...O hydrogen bonding of exchangeable type.

Moreover some characters of OH groups of easily exchangeable type are inferred from Figures 8.2, 8.3, 8.4 and 8.8. In these Figures the shifting of band due to OH stretching vibration at 3340 to 3320 cm^{-1} did not be observed in deuterated PVA film, while the band due to OH stretching vibration of complex was shifted to the higher wave number with deuteration. This fact means that only OH...O hydrogen bonding appearing at 3340 to 3320 cm^{-1} is exchanged to OD through deuteration and OH...O stretching vibration at 3380 dose not be exchanged. This fact supports the results obtained in the former discussions.

8.3 Summary

Mechanism of bonding between PVA and montmorillonite is directly clarified by employing the means of combination of infrared absorption techniques with deuteration exchange.

Results show that the mechanism of bonding is OH...O hydrogen bonding formed between OH groups of PVA and oxygen atoms of silica-tetrahedral layers of montmorillonite and the distance between two oxygen atoms in this hydrogen bonding is 2, 83 Å , it is a little longer than that in PVA molecules which takes the value of 2.77 to 2.80 Å.

CHAPTER 9

CONCLUSION

In this thesis the following four subjects were investigated :

- 1) Phenomena brought by the association of montmorillonite with polyvinyl alcohol in water suspension. In the course of discussion the behaviour of montmorillonite in water suspension was also dealt with.
- 2) Relations between a physical property of dried polyvinyl alcohol-montmorillonite complex and the existing state of the polymer in the complex.
- 3) Bonding mechanism between polyvinyl alcohol and montmorillonite.
- 4) Tests of the older investigating method and the development of new method.

The most important results obtained from these investigations are summarized as follow :

- 1) In polyvinyl alcohol-montmorillonite-water system, flocculation of clay particles brought by the construction of interparticles bridges of polymer molecules.
- 2) Kinetic unit of montmorillonite in water suspension is particle in which infinite number of unit layers are involved.
- 3) Calcium montmorillonite prepared from sodium montmorillonite suspension has large basal spacing before drying and after drying this expansible character is lost.
- 4) A routine centrifugal method using for the determination of amount of polymer adsorbed from clay-polymer solution system was tested with new method devised by the author and it was clarified that the centrifugal method gives wrong results.
- 5) Kinetics of thermal degradation of polyvinyl alcohol in complex and in mixture with clay were studied. Energy of activation of thermal degradation of polyvinyl alcohol in free state and adsorbed

on clay surface are 50 K cal/mol and 31 K cal/mol, respectively. Order of reaction of thermal degradation of polyvinyl alcohol in free state and adsorbed on clay surface are 1.6 and 1.0, respectively.

6) By using DTA technique, polyvinyl alcohol in complex is analysed separately according to its existing state.

7) A relationship between the degree of polymerization of polyvinyl alcohol (P) and points at which the stereo hindrance of polymer adsorption appears remarkably A is presented by following equation

$$A = C (P)^{-1/3} \quad C ; \text{ constant}$$

where A is presented as gram of polymer per 100 grams of clay used.

Changes in number of adsorbed points from solution (N_1) to dry state (N_2) in polyvinyl alcohol-bentonite complex is presented by below equation

$$(N_1) / (N_2) = C (P)^{0.3}$$

where C is proportional constant.

8) Polyvinyl alcohol adsorbed onto outer surface of montmorillonite play an important role on water stability of complex of polyvinyl alcohol-Bentonite.

9) The bonding mechanism between polyvinyl alcohol and montmorillonite has been firstly clarified by using infrared absorption technique. It is hydrogen bonding between OH groups in polyvinyl alcohol and Oxygen atoms of silica-tetrahedral layers of montmorillonite.

Studies on the organic clay systems must be further developed, because many investigators begin to know the importances of these systems in their fields.

In the course of their investigations, the investigating methods

devised in this studies would play an important roles.

ACKNOWLEDGEMENT

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