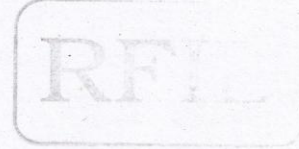


EGE ÜNİVERSİTESİ
MERKEZ KÜTÜPHANESİ

EGE UNIVERSITY GRADUATE SCHOOL OF NATURAL AND
APPLIED SCIENCES

(MASTER THESIS)



ADSORPTION OF POLYVINYLPIRROLIDONE

ON CLAY MINERALS

Lina ISRAEL

Chemistry Department

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Supervisor: Prof. Dr. Çetin GÜLER

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III

"Kil Mineralleri Uzerinde Polivinilpirolidon Adsorpsiyonu" adlı bu çalışma, "Lisansüstü Eğitim ve Öğretim Yönetmeliği"nin 12 inci madde (c) ve (d) bentleri ve Enstitü yönergesinin ilgili hükümleri dikkate alınarak tarafımızdan değerlendirilmiş olup yapılan sözlü savunma sınavında aday oy...birliği.. ile başarılı bulunmuştur. Bu nedenle Lina FRANKO'nun sunduğu metnin yüksek lisans tezi olarak kabulüne oy...birliği ile karar verilmiştir.

14 Ocak 1999

Jüri Başkanı: Prof. Dr. Çetin GÜLER

Raportör ; Prof. Dr. Devrim BALKÖSE

Üye ; Prof. Dr. Aysel TEMİZER

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Süleyman BORUZANLI

Enstitü Sekreteri

Prof. Dr. İsmet ERTAŞ

Enstitü Müdürü

V

ÖZET

POLİVİNİLPIROLİDONUN KİL MİNERALLERİ ÜZERİNDEKİ ADSORPSİYONU

İSRAEL, Lina

Yüksek Lisans Tezi, Kimya Bölümü

Tez Yöneticisi: Prof. Dr. Çetin GÜLER

Ocak 1999, 58 sayfa

Bu tezde, polivinilpirolidonun kaolinit ve montmorillonit gibi kil mineralleri üzerindeki adsorpsiyonu incelenmiştir.

Adsorpsiyon izotermi H-tipidir. Sıcaklık ve pH' ın adsorpsiyon üzerindeki etkisi azdır. Kaolinit üzerinde adsorpsiyon yüzeyde gerçekleşirken, montmorillonit üzerinde adsorpsiyon tabakalar arasında gerçekleşmiştir.

Anahtar sözcükler: Polivinilpirolidon, adsorpsiyon, kaolinit, montmorillonit.

VII

ABSTRACT

**ADSORPTION OF POLYVINYLPIRROLIDONE ON
CLAY MINERALS**

ISRAEL, Lina

Msc in Chemistry Department

Supervisor: Prof. Dr. Çetin GÜLER

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In this thesis, adsorption of polyvinylpyrrolidone on clay minerals such as kaolinite and montmorillonite are studied.

Adsorption isotherms are H-type. Temperature and pH on adsorption are not very effective. The adsorption of polyvinylpyrrolidone on kaolinite occurs on surface while the adsorption on montmorillonite occurs in the interlayer.

Keywords: Polyvinylpyrrolidone, adsorption, kaolinite, montmorillonite.

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1. INTRODUCTION

Polymers, soluble in water has had a lot of uses in recent years. Therefore, the production of polymers is increasing day by day. For example, polymers (especially polyvinylpyrrolidone) are used in textiles, dyes, cosmetics, toiletries, pharmaceuticals, detergents, shampoos etc. . Even, in refining of water polymers are chosen.

Polyvinylpyrrolidone was first used (about 1940 in Germany) as a blood plasma extender, and it is now widely used as a pigment dispersant, as a bonding agent, and a film-former. As a film-former it is commonly found in aerosol hair sprays (Francis, 1973).

Polyvinylpyrrolidone which is used in many fields will possibly be transferred to soil, lakes, seas, and subsoil water with churns or refined liquid part even after refining. Transportation to soil is done with clay minerals. Therefore, adsorption of polyvinylpyrrolidone on clay minerals and the description of adsorption mechanism are very important.

In this study, kaolinite and montmorillonite are used for polyvinylpyrrolidone adsorption.

2. CLAY MINERALS

To most of us the word 'clay' usually means a fine-grained material which when mixed with water becomes extremely plastic and mouldable. Yet clays have a much wider impact on our lives than many of us commonly realize. They form an important constituent of soils, where they exert a dominant influence on soil structure and plant nutrition. Clays are used for brick-making, as fillers and coating agents in paper manufacture, and of course in ceramics. Their properties are complex and of great scientific interest, as indicated by the enormous amount of research on clays which has been undertaken by geologists, mineralogists, chemists, engineers and others over a considerable period of time.

The term 'clay' is often (e.g. in soil mechanics) used in the restricted sense of a particle-size classification term for the natural constituents of soils and sediments. In this usage, clays describe a chemically very heterogeneous and structurally complex assemblage of colloidal particles, having mean diameters ranging from a few microns (μm) down to a few hundredths of a micron. Chemically, this complex assemblage consists of a considerable quantity of hydrous aluminium silicates, with lesser amounts of finely divided quartz, feldspars, carbonates, oxides and hydroxides (mainly

of aluminium and iron) and organic matter. 'Clay minerals' refers to the group of fine-grained hydrous silicates of aluminium (and also to some extent of magnesium or iron). When examined under the scanning electron microscope, these materials are seen to consist of readily identifiable particles, which can have a variety of geometric shapes (flat or crincky plates, ribbon, tubes or pods). Despite this variety of morphology, clays are closely interrelated in terms of their basic crystal structures, and also in the characteristic physical and chemical properties resulting from their crystal chemistry.

2.1 Structure and Chemistry of Clay Minerals

The crystal structures and chemical compositions of the clay minerals, and their associated minerals, are not discussed extensively. By way introduction, it is merely noted that there are two basic building blocks common to soil clay mineral structures:

1. A sheet of silicate tetrahedra, consisting of two layers of oxygen atoms, and containing silicon in four-fold (tetrahedral) coordination.
2. An octahedral sheet, consisting of two layers of oxygen atoms or hydroxyl groups, between which aluminium, magnesium or iron are bounded in six-fold coordination. If the

layer contains mainly trivalent aluminium ions which occupy two-thirds of the available octahedral interstices, this is known as a gibbsite-type or dioctahedral layer. Conversely, if the layer contains mainly divalent magnesium ions, these will occupy all of the octahedral sites, and the layer is called a brucite-like or trioctahedral layer.

The structural units of clays therefore consist of either alternating tetrahedral or octahedral sheets (OT or 1:1 structure), as in the kaolinite group of clay minerals; a sandwich of one octahedral sheet between two tetrahedral sheets (TOT or 2:1 structure), as in illite and smectite clay minerals, of which the most common is montmorillonite; or an arrangement in which the three-layer TOT units alternate with a brucite layer (2:1:1 structure), as in chlorite.

2.2 Classification of Clay Minerals

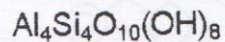
Clay minerals are classified as follows:

1. Kaolinite group minerals.
2. Serpentine group minerals.
3. Smectite group minerals.
 - a. Dioctahedral.
 - b. Trioctahedral.
4. Illite/mica group minerals.
5. Chlorite group minerals.

6. Vermiculite group minerals.
7. Interstratified or mixed layer minerals.
8. Sepiolite and palygorskite.

2.2.1 Kaolinite group minerals

These consist of uncharged, dioctahedral layer units with a 1:1 structure of 7A° in thickness and of formula :



The individual mineral species considered are:

1. Kaolinite itself, which has varying degrees of crystallinity and a distinct platy form (Figure 2.1).
2. Dickite, which is similar to kaolinite, but with a different stacking arrangement of the unit layers.
3. Halloysite, which consists of a poorly ordered arrangement of kaolinite-like units, with a variable amounts of water between the layers, generally between 0.6 to 4 H_2O per formula unit, and often with a tubular form.

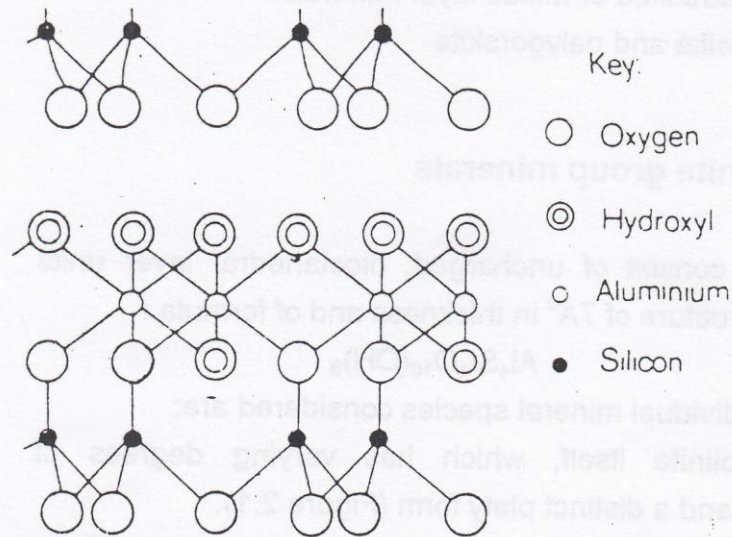


Figure 2.1 The layer structure of kaolinite along the a-axis (Theng, 1979).

The inability of kaolinite crystals to show interlayer (intracrystalline) expansion or swelling is indicative of strong interlayer bonding. The forces holding the layers together have been attributed to O-H ...O hydrogen bonding (involving 4 out of 6 hydroxyls per unit cell) through the superposition of oxygen and hydroxyl planes of successive layers, amplified by van der Waals attraction.

Summation of anionic and cationic charges in the structure depicted in figure 2.1, shows that the kaolinite layer is electrically neutral. In reality, however, most if not all kaolinites carry a net negative surface charge, the origin of which is still a matter of some controversy. The problem relates to the fact that any isomorphous replacement which might occur is limited in extent and so can not be readily deduced from analytical chemical data. Kaolinite may carry a small amount of pH-dependent negative charge due to exposed silica as well as positive charges on the edge or cleavage face of the crystal ascribable to exposed alumina.

It is widely recognised that the edge surface of kaolinite and of layer silicates, in general, may acquire negative and positive charges depending on the pH of the medium (van Olphen et al., 1963). The former may arise through dissociation of silanol groups under alkaline conditions and the latter through protonation of edge aluminols at acid pH values. These points are illustrated in figure 2.2.

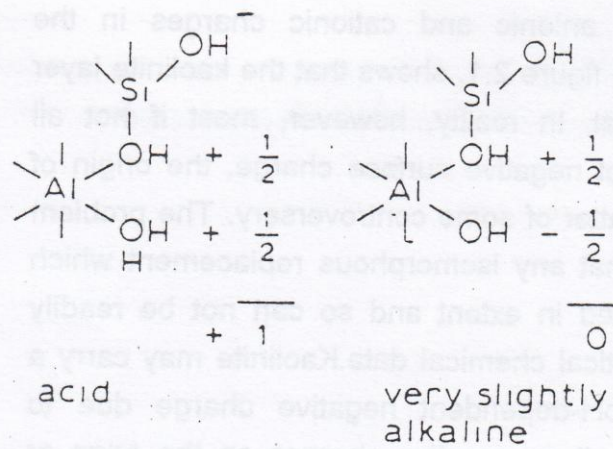
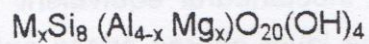


Figure 2.2 Variations in charge characteristics of the edge surface of kaolinite-type crystals under acid and alkaline conditions (Schofield, 1953).

2.2.2 Smectite group minerals

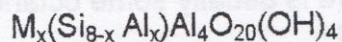
These have a dioctahedral or trioctahedral 2:1 layer structure, with isomorphous substitution leading to a negative layer charge of less than 1.2 per formula unit. As with vermiculite, this charge is compensated for by interlayer exchangeable cations. Layer spacings vary between 10 and 15 Å, and are generally dependent on the nature of the exchangeable cation and the relative humidity. Smectites nearly always occur in a fine-grained particles of clay size. The main dioctahedral minerals are :

1. Montmorillonite, which is predominantly octahedrally charged, with an ideal general formula of :



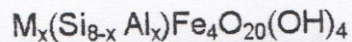
where M represents the exchangeable cation. It should be stressed that this formula is ideal and that in practice montmorillonite usually exhibits some tetrahedral substitution and also contain some octahedral ferric iron. Tetrahedral substitution should always amount to smaller than 50 % of the total charge deficit.

2. Beidellite, which is predominantly tetrahedrally charged and contains more aluminium and less magnesium than montmorillonite. The ideal formula is:



Again, the real situation is that the composition of beidellite is somewhat variable, but nevertheless tetrahedral substitution should always account for greater than 50 % of the total charge deficit.

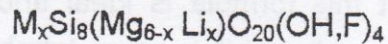
3. Nontronite, which is iron-rich smectite with an ideal formula of :



Few nontronites actually have this compositions. Octahedral substitution is common, but does not account for greater than 50 % of the total charge deficit. Some nontronites are known where Si is substituted for by Fe^{3+} in the tetrahedral sheet .

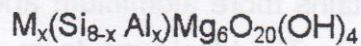
The main trioctahedral smectites are as follows:

4. Hectorite, trioctahedral 'equivalent' of montmorillonite in that, ideally, the layer charge arises only from octahedral substitution, as in the following formula:



As seen above, lithium and fluorine are essential constituents of hectorite.

5. Saponite is again a magnesium-rich clay, but because it is tetrahedrally substituted it is more closely related to beidellite. The ideal formula for saponite is:



but in practice there is usually some octahedral substitution of Mg, usually by Fe^{3+} .

2.3 Properties of Clay Minerals

2.3.1 Ion exchange

One of the fundamental properties of clays is the electrical charge on their unit particles which means that clays will sorb cations or / and anions that neutralize the layer charge, but which are exchangeable. This means that they can readily be replaced by the other anions or cations when brought into contact with these ions in aqueous solution (Grim, 1968).

Except under extremely acidic conditions, the layer charge is predominantly negative, a fact which may be verified by investigating the electrochemical properties of dilute, aqueous dispersions of clay (Swartz-Allen, 1974). This means that clays tend to sorb cations, and are said to have a certain cation exchange capacity, or CEC, which can be expressed as a certain number of chemical equivalents per unit weight of dry clay (normally quoted in milliequivalents per hundred grams).

Smectites contain extensive isomorphous substitution of this kind, and frequently have CEC values greater than 100 milliequivalents / 100 g. Their exchange cations are mainly between the adjacent tetrahedral layers. Depending on the relative humidity (or, in contact with a liquid, the ionic concentration) smectites may adsorb water and hydrate, the crystal lattice swelling in a direction perpendicular to the plane of the surface oxygens. However, neither the CEC of a clay nor the degree of swelling it can accommodate is simply related to the amount of isomorphous substitution. Other clays have much less isomorphous substitution correspondingly lower CEC values. It has been suggested that broken bonds at particle edges may also contribute to exchange capacity, particularly for clays of the kaolinite group. However, there is considerable evidence to suggest that, except under fairly

alkaline conditions, the charges due to the edge defects are positive, leading to anion rather than cation adsorption at these sites. There are two possible mechanisms for creation of positive edge charges:

1. Protonation of exposed Al-OH groups.
2. The dissolution of some of the clay at pH less than 4 followed by edge adsorption of aluminium ions.

The negatively charged clay surfaces do not have an equal affinity for all cations, but in fact exhibit a selectivity which depends upon such factors as the ionic charge, size and state of hydration of the cations. In general, cation-exchange selectivity increases with cation charge and increases with ionic radius. Bivalent ions and polyvalent ions are in general quite strongly adsorbed. Also some monovalent ions are strongly adsorbed and permit only limited swelling on account of their large sizes and relatively low hydration energies.

Ion exchange reactions in clays are important for a number of reasons:

1. As a source of nutrients in soils for plant growth. This particularly applies to calcium, magnesium, and potassium ions, although there is some evidence that plants can utilize

potassium in soils even when it is present in a non-exchangeable form (Newman,1984).

2. The mechanical properties of a clay soil (strength, yield point, plasticity) strongly depend upon whether Na^+ or Ca^{2+} is the principal counter-ion present (Grim ,1968).

3. Ion exchange processes may play a role in the immobilization of undesirable cations such as organic pesticides or components of radioactive wastes.

2.3.2 Interaction of organic matter with clay minerals

Many organic molecules, like water can be readily adsorbed by clay minerals. In some cases, particularly for non-polar organic molecules, the interaction forces are relatively weak, corresponding with physical adsorption only. However, polar or ionic organic species can enter into a wide variety of chemical reactions to form complexes with clay minerals. Smectites, vermiculite and kaolinite group minerals can be expanded by penetration of such molecules between the unit layers to form an intercalation complex. Depending on the nature of the organic species, the bonding in organo-clay complexes occur via:

1. Hydrogen bonding.

2. Ion-dipole forces, including formation of coordination complexes to exchangeable cations.
3. Bonding via 'water bridges' between organic molecules and hydrated cations.
4. Cation exchange.
5. Anion exchange.
6. d- π bonding between adsorbed arenes and transition-metal exchange ions.

2.3.2.1 Intercalation complexes of kaolinite

In kaolinite, there are a number of polar organic molecules, and some organic salts which are able to disrupt the interlayer bonding between the adjacent siloxane hydroxyl-aluminium surfaces, and to penetrate the interlayer space to form a complex by hydrogen bonding to both surfaces. The interlayer spacing of kaolinite, normally 7Å , can be expanded in this manner to 10Å or more, depending on the identity of the guest molecule.

2.3.2.2 Intercalation complexes of montmorillonite

Neutral, polar organic molecules which are miscible with water, can replace water in the interlamellar space of

montmorillonite, being either coordinated to exchange cations or held more loosely between cation solvation sheaths. These complexes can be prepared by reacting montmorillonite with the organic species in either liquid or vapour form. In many cases, these complexes form a well-ordered structure which can be determined by X-ray or neutron diffraction.

2.3.2.3 Ionic organic species

Organocations, can replace the inorganic exchange cations of smectites, and are strongly bound, producing an interlayer space which is organophilic in character, and swells little in water, but may swell extensively in polar organic solvents. Neutral amines may similarly be adsorbed, and may protonate in the interlamellar space. (Fripat et. al.,1965).

In contrast to organocations organic anions are adsorbed at particle edges, and can be efficient peptizing agents when they promote charge reversal. They are widely applied in oilfield drilling fluids (van Olphen, 1977).

2.4 Uses of Clay Minerals

2.4.1 Uses of kaolinite group minerals

Kaolinite is used in paper industry as a coating and filling agent and also for pottery and porcelain manufacture. Sometimes, it is used as extenders in paints, plastics and rubbers. In the paper industry, the particle size and brightness of kaolinites are important, the latter being adversely affected by small quantities of iron impurities.

2.4.2 Uses of smectites

Smectites have numerous industrial uses, of which the most important are:

1. In foundaries, as a binding agent in the preparation of moulding sands.
2. As a backfill in radioactive waste repositories.
3. As a catalyst in various hydrogenation reactions.
4. In civil engineering, to hinder the movement of water or chemical wastes.

3.ADSORPTION

Adsorption, is a process in which atom, molecule or ion of a solute is assembled on a solid surface in gas, vapour, liquid phase or in a solution. The compound that is adsorbed is known as the adsorbate, and the material that provides the adsorbative properties is known as the adsorbent. By definition, the process of adsorption is limited to the surface of a material, bulk penetration of one material by another being known as absorption. The phenomenon of adsorption can occur at all surfaces, and five types of interface can exist: gas-solid, liquid-solid, liquid-liquid, solid-solid, gas-gas. The gas-solid interface has probably received the most attention. The liquid-solid interface is now receiving much attention because of its importance in many electrochemical and biological systems, but the nature of the interface is imperfectly understood on atomic scale, primarily because of lack of suitable techniques for investigating the adsorption phenomenon (Hair,1967).

Adsorption depends on several factors such as the nature of substrate, solvent, adsorbate species, temperature and even mode of mixing. Several interactions such as electrostatic attraction, covalent bonding, hydrogen bonding or non-polar interactions between the adsorbate species, and

lateral interaction between the adsorbed species as well as their desolvation can contribute to the adsorption process (Somasundaran, 1997).

3.1 Classification of Adsorption

The adsorption process is nearly always exothermic. Many heats of adsorption have been measured. These measurements indicate that there are in general, two distinct types of adsorption that can be differentiated. The first type, known as physical adsorption or physisorption, is a process in which the bond between the adsorbent and the adsorbate is thought to be of van der Waals type. Because this bond is very weak, it is characterized by a low heat of adsorption usually of the order 10-20 J / mole. This value is of the same order of magnitude as the heat of vaporization of the adsorbate and lends credence to the concept of a weak 'physical bonding'. Physical adsorption is usually observed at low temperatures or on relatively 'inert' surfaces.

The second type of adsorption that is observed is known as chemical adsorption or chemisorption. In this case the adsorbate undergoes a strong chemical interaction with the unsaturated surface and gives rise to a high heat of adsorption usually of the order of 60-200 kJ / mole. Chemical

adsorption is often characterized by taking place at elevated temperatures and is often an activated process. It may be dissociative, nondissociative, or reactive in nature.

3.2 Adsorption Isotherms of Small Molecules

The amount of gas that is physically adsorbed on a solid surface is a function of both the temperature of the system and the partial pressure of the adsorbate.

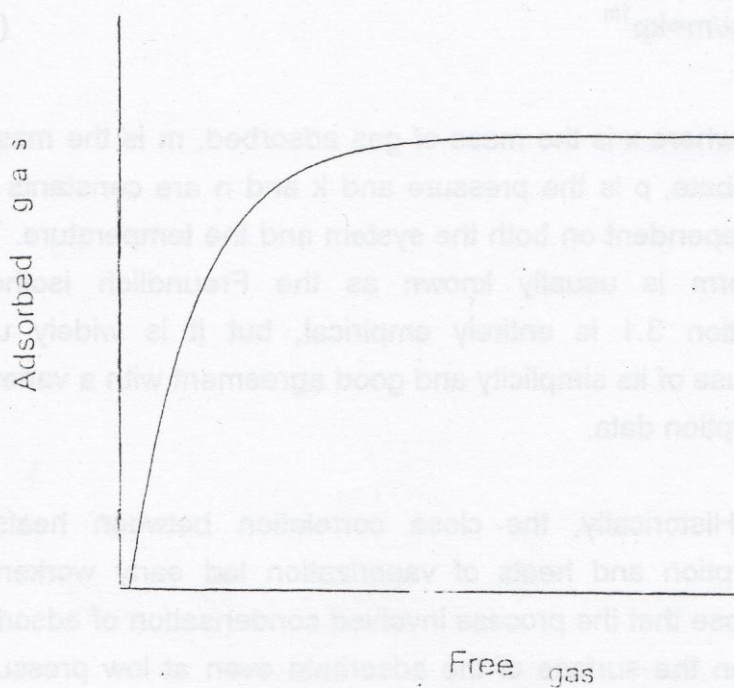


Figure 3.1 Adsorption of a gas on a solid.

In figure 3.1 the amount of gas adsorbed on a solid is plotted as a function of free gas. As would be expected for a weak van der Waals type of bond, the amount of gas adsorbed is directly related to the pressure and inversely related to the temperature. This type of graphical representation is known as an adsorption isotherm, and many mathematical interpretations of adsorption isotherms have been given. One of the best known of this is an empirical equation of the form

$$x/m = kp^{1/n} \quad (3.1)$$

where x is the mass of gas adsorbed, m is the mass of adsorbate, p is the pressure and k and n are constants that are dependent on both the system and the temperature. This isotherm is usually known as the Freundlich isotherm. Equation 3.1 is entirely empirical, but it is widely used because of its simplicity and good agreement with a variety of adsorption data.

Historically, the close correlation between heats of adsorption and heats of vaporization led early workers to suppose that the process involved condensation of adsorbing gas on the surface of the adsorbate even at low pressures. Langmuir, however pointed out that this concept was unlikely

due to the rapid fall of intermolecular forces with distance, and he introduced the idea of monomolecular films. In this approach the adsorption process is considered to be an equilibrium process in which the rate of molecules hit a surface and are adsorbed is equal to the rate at which molecules of gas are desorbed from the surface.

If the fraction of surface covered with the adsorbed gas at any time is θ and if the heat of adsorption is assumed to be independent of the surface coverage, the rate of desorption is proportional to the surface coverage:

$$R_{\text{des}} = k_1 \theta \quad (3.2)$$

Now, if μ is the rate at which gas molecules strike the surface and α is the fraction of these molecules that stick on the surface for an appreciable length of time (i.e., are adsorbed), then the rate of adsorption is proportional to the fraction of surface that is not covered by gas molecules and is given by

$$R_{\text{ads}} = (1-\theta) \alpha \mu \quad (3.3)$$

At equilibrium,

$$R_{\text{ads}} = R_{\text{des}} \quad (3.4)$$

Therefore,

$$k_1 \theta = (1 - \theta) \alpha \mu \quad (3.5)$$

The rate at which the molecules strike the surface, μ , proportional to the pressure P , and so

$$\mu = k_2 P$$

Therefore,

$$\theta = k P / (1 + k P) \quad (3.6)$$

where $k = k_2 / k_1$. This known as the Langmuir isotherm.

At very low pressures equation 3.6 reduces to $\theta = k P$ this is a restatement of Henry's law, and constantly this part of the adsorption isotherm is often known as Henry's law region. At high pressures θ approaches 1 and indicates monomolecular coverage. At intermediate pressures one might expect an expression that is intermediate between

$\theta = 1$ and $\theta = k P$ to hold, i.e., an expression of the type

$$\theta = k P^{1/n} \quad (3.7)$$

where n is more than 1. This can be compared with equation 3.1 and is seen to be identical with Freundlich equation.

3.3 Adsorption of Polymers

A feature common to both aqueous and non-aqueous systems is that a large number solvent molecules must be desorbed in order to accommodate a single polymer molecule. The translational entropy so gained by the system provides the driving force for polymer adsorption (Figure 3.2). Such entropy effects are also partly responsible for the very strong attachment of polymers despite the very small or virtually zero enthalpy change of the adsorption process.

The adsorption of polymers at the solid-liquid interface depends on several factors such as the nature of substrate, solvent, adsorbate species, the presence of secondary competing-cooperative species, temperature, and even the mode of mixing. Polymer adsorption in aqueous media is

controlled by the polymer charge, molecular weight, solvent, solution conditions (pH, ionic strength), and porosity of substrate (Somasunduran, 1997).

The rate of adsorption of a polymer is determined by several processes such as:

1. The transport of the molecules from bulk to the interface by diffusion.
2. A reconfiguration process during the attachment to the interface.
3. Exchange processes between polymer molecules of different mass (Lipatov, 1982).

The mechanisms underlying the reactions of simple organic compounds with clays are now fairly well-understood and this basic information is of much value to the interpretation of clay-polymer complex formation. Thus, positively charged organic micromolecules are adsorbed by an exchange reaction with the charge-balancing inorganic cations at the clay surface, and uncharged polar compounds principally by interaction between the functional group and the exchangeable cation. Adsorption is normally exothermic and increases with molecular weight of the compound, reflecting the increased contribution of van der Waals forces to the overall adsorption energy.

Although these principles would apply to the adsorption of organic macromolecules, their interactions with clays differ in some important respects from those of simple non-polymeric species. These differences essentially arise from the fact that besides being long, a polymer chain is flexible and often polyfunctional. Chain flexibility and polyfunctionality further allow the polymer to adopt various shapes or conformational states at the surface and to be attached to the solid by numerous segment-surface bonds. A complete quantitative description of polymer behaviour at the solid-solution interface would therefore require a knowledge of both the solution and the surface properties of the polymer.

There are three possible bonding mechanisms through which a nonionic polymer is attached to a clay surface:

1. Ion-dipole interaction, in which metal-ligand bonding exists between exchangeable cation.
2. Bonding through a water bridge to the exchangeable ion.
3. Attachment of polymer segments to the surface of the clay (Greenland, 1965).

3.3.1 Adsorption isotherms of polymers

The determination of adsorption isotherms is perhaps the most useful, single technique or approach for characterising the properties of polymer solutions in the presence of adsorbing surface. The determination of adsorption isotherms can only yield a limited amount of information about state of the adsorbed layer.

A feature of polymer adsorption is that equilibrium conditions may take a considerably long time (>100 s) to become established. This is particularly true when porous adsorbents, such as clays are used. In the case of micromolecules, the shape of the isotherm is diagnostic of the mechanism underlying the adsorption process. Thus, on the basis of the initial slope, Giles et al. (1960) have been able to distinguish four classes or types of solid-solution adsorption (SSA) isotherms, referred to as S, L (for 'Langmuir'), H (for 'high affinity'), and C (for 'constant partition') (Figure 3.2).

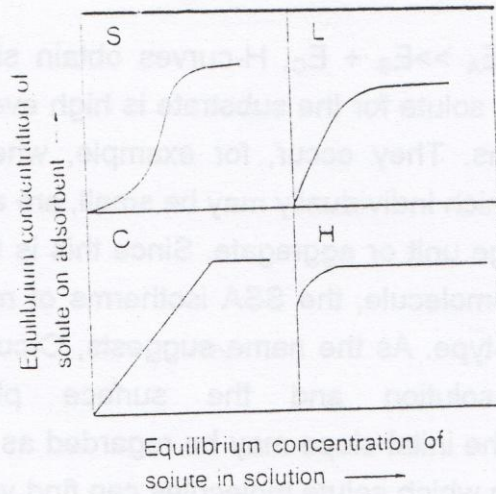


Figure 3.2 The different classes or types of solid-solution adsorption isotherms according to Giles et. al. (Theng, 1979).

S-type isotherms are rarely encountered with polymer systems. They occur when the activation energy for removal of the adsorbed species (E_A) is concentration dependent and/or is reduced by a large negative contribution from that of the solvent (E_B), or from a second solute (E_C) if present. L-curves are found in situations where none of these energy terms is dependent on concentration.

When $E_A \gg E_B + E_C$, H-curves obtain since here the affinity of the solute for the substrate is high even at very low concentrations. They occur, for example, when the solute molecules which individually may be small, are adsorbed as a relatively large unit or aggregate. Since this is the case for a single macromolecule, the SSA isotherms of most polymers are of the H-type. As the name suggests, C-curves between the bulk solution and the surface phase during adsorption. The initial slope may be regarded as a measure of the ease with which solute molecules can find vacant sites on the surface. The increase in slope with concentration for S-type isotherms indicates that there is a corresponding rise in the number of adsorbing sites. On the same basis, the decrease in slope for L-curves may be ascribed to greater difficulty the solute has in finding surface vacancies as its solution concentration is increased. Experimentally, the SSA isotherms for a number of polymers are of the L-type particularly when they are measured at low concentration and surface coverage. The constancy in slope shown by the C-curves, would indicate that the number of adsorbing sites does not vary with concentration. This implies that new sites are being created as adsorption progresses. Only porous adsorbents seem capable of giving rise to linear isotherms. As the solute penetrates the solid structure through a micropore, more sites become exposed and accessible to the following molecules.

Adsorption isotherms of polymers are determined similar to those for surfactants, i.e. by measuring depletion of polymer concentration in solution after contact with the solid. Linear flexible macromolecules can assume different conformations at the interface and also exhibit varying degrees of attachment to the surface (Napper, 1983).

At the solid-liquid interface the macromolecules usually prefer a conformation that allows a maximum segment-surface contact. Since the attachment of one segment will increase the probability of neighboring segments to be adsorbed and the number of functional groups per molecule is large, multiple bonding between the polymer and surface is favoured. The result is normally an interfacial conformation consisting of alternating with free three-dimensional 'loops' extending away from the surface and with the chain terminating at either end in two-free dangling 'tails'.

4. POLYVINYLPIRROLIDONE

Polyvinylpyrrolidone (PVP) is a hygroscopic white solid available in molecular weights from 10000 to 600000 g / mole (Figure 4.1).

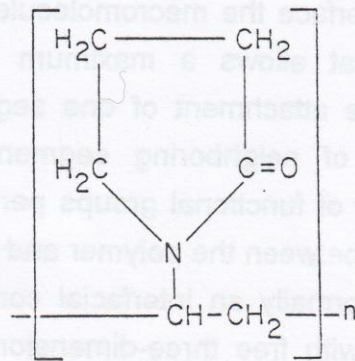


Figure 4.1 The molecular structure of PVP (Francis, 1973).

It is soluble in cold water and in many organic solvents. Its solubility is limited by the viscosity of the solution. Dessicated to less than 0.5 % H₂O, it can be dissolved in ketones and dioxane to give 10-50 % solutions. The powder is quite stable to heat (up to 120°C) and can be stored under ordinary conditions without decomposition or degradation.

Because PVP has a high dielectric constant adsorption through cation-dipole interaction would be a possible mechanism (See 3.3).

The bonding mechanism of PVP has been detected by IR technique. If the bonding on PVP were through a water bridge, the shift in carbonyl stretch frequency should be weaker than that due to the interaction with counter-ion. (Parfitt, 1968). But the intensity in carbonyl stretch $1655-1685\text{ cm}^{-1}$ of PVP is strong and is close to the OH deformation of adsorbed water ($1625-1655\text{ cm}^{-1}$).

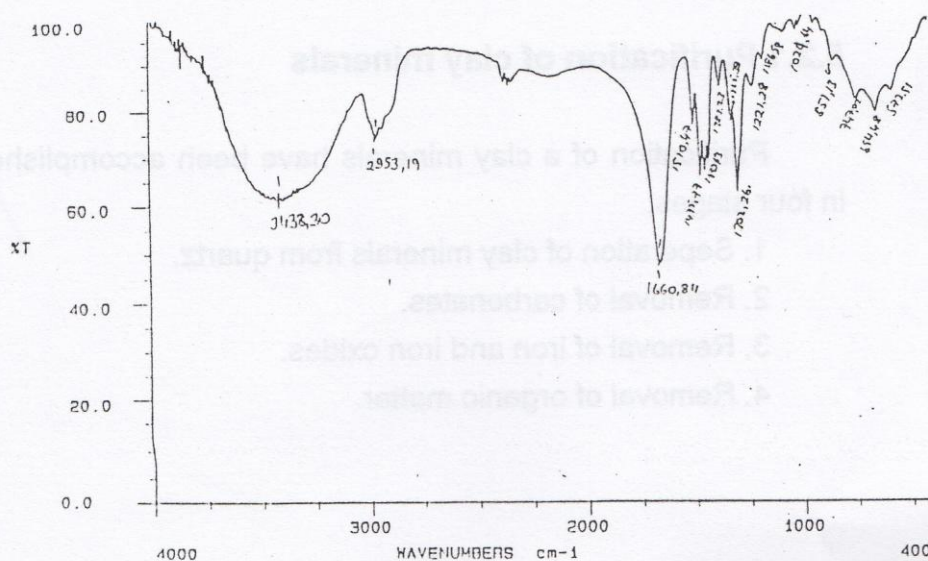


Figure 4.2 IR spectrum of PVP

5. MATERIALS AND METHOD

5.1 Materials

PVP (Sigma) with two different molecular weights 44000 (K 30) and 600000 g / mole (K 80-100) was used.

5.2 Method

This method consists of two stages. In the first stage purification of clay minerals is carried out while in the second, PVP adsorption on the clay minerals are observed.

5.2.1 Purification of clay minerals

Purification of a clay minerals have been accomplished in four stages.

1. Separation of clay minerals from quartz.
2. Removal of carbonates.
3. Removal of iron and iron oxides.
4. Removal of organic matter.

5.2.1.1 Seperation of clay minerals from quartz

Clay particles have been separated according to their size via sedimentation. The basic principle of sedimentation is, in a medium (liquid / gas) if the weight of the clay particle is greater than floatation force, the particles will settle down. Particles must be either in a great size or must be denser to sediment. Clay minerals are not pure (they contain quartz) so sedimentation is applied on, for separation according to particle size. Hydrous aluminium silicates smaller than 2 μm in diameter is called as clay minerals. To collect particles smaller than 2 μm , Stokes law is applied.

$$R = \left[\frac{18\eta h}{(d_{\text{clay}} - d_{\text{water}})gt} \right]^{\frac{1}{2}} \quad (5.1)$$

In equation 5.1 η indicates viscosity of water, h is the height of water, t is the time, d_{clay} is the density of clay mineral, g is the gravitation force, and r is the radius of the clay mineral.

3 kilograms of clay is put in a deep flask and 13 or 14 liters of distilled water is added. This dispersion is mixed about two hours with a mechanic mixer. The liquid at the

upper part is poured. A little amount of the liquid is taken from the remainder mixture to 2 or 3 litered flasks. Distilled water is added and mixed about 30 minutes. If particles smaller than $2 \mu\text{m}$ in diameter are to be collected then the height of the water should be 15,6 cm and the time should be 30 hours according to the equation 5.1. Then the particles needed are taken to another flask and are put in a 105°C oven to dry.

5.2.1.2 Removal of carbonates

The first thing has to be done while removing carbonates is to find out if the clay mineral is formed either from dolomite or from lime-stone. To understand this, pour one or two droplets of 0.5 N acetic acid on the clay mineral. If there is not a reaction carbonate is originated from dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$) because dolomite does not decompose with weak acids. If there is a reaction, the clay mineral is originated from lime-stone (CaCO_3). At this point, 300 ml of distilled water is put on 50 g of clay mineral and 0,25 N 1 L of acetic acid is added. This dispersion is mixed until all CO_2 gas is removed with a mechanic mixer. At last, the mixture is put in a 105°C oven to dry.

5.2.1.3 Removal of iron and iron oxides

The best way to remove iron and iron oxides is to boil up the clay mineral and oxalic acid with aluminium plates. 750 ml of distilled water is put on 50 g of clay mineral and 37.5 g of oxalic acid is added. Aluminium plates are put inside the mixture and the mixture is boiled up. Iron and iron oxides are held on aluminium plates. This process is carried out until iron and iron oxides are not held on aluminium plates. The mixture is put to filtrate for one night, and is filtered with blue filter paper. Then, the clay mineral is put in a 105°C oven to dry.

5.2.1.4 Removal of organic matter

At this stage, clay mineral is without carbonates, but acidic. It is wetted with sodium acetate buffer which makes easier to react the clay mineral with H_2O_2 . Humic compounds can be formed in the presence of calcium salts which make organic compounds oxide with H_2O_2 and can be removed. 75 ml of 30 % H_2O_2 is put on 50 g of clay mineral. The mixture is kept in a cold medium for the reaction to continue without evaporation. When the reaction ends the mixture is heated and then put in an oven to dry at 105°C.

5.2.2 Sodium saturation of clay minerals

The clay mineral is saturated with sodium ions before adsorption. 1 N 1 L of NaCl is put on 100 g of clay mineral and is mixed for 5 days. After mixing, mixture is filtrated and washed until chloride ions can not be detected.

5.2.3 Analytical determination of PVP

The non-adsorbed PVP concentration in the supernatant was determined using a Shimadzu 160A spectrophotometer ($\lambda = 271 \text{ nm}$).

5.2.4 Adsorption of PVP on sodium kaolinite

PVP solutions with concentrations between 50 ppm and 5000 ppm were prepared. Equal volumes of Na-kaolinite dispersions and PVP solutions were mixed at constant temperatures (20°C , 25°C , 30°C , 35°C , 40°C). The concentration of Na-kaolinite in the adsorption experiments was 5 gL^{-1} . The amount of PVP adsorbed was calculated from the difference between total added PVP and the PVP concentration in the supernatant after centrifugation (90 minutes at 7000 rpm).

5.2.5 Adsorption of PVP on sodium montmorillonite

PVP solutions with concentration of 5000 ppm and 66000 ppm were prepared. Equal volumes of Na-montmorillonite dispersions and PVP solutions were mixed at 20 °C. The concentration of Na-montmorillonite in adsorption was 1 gL⁻¹. The amount of PVP adsorbed was calculated in the same way as Na-kaolinite (See 5.2.4).

The experiments mentioned above were done in the same arrangement shown schematically below.

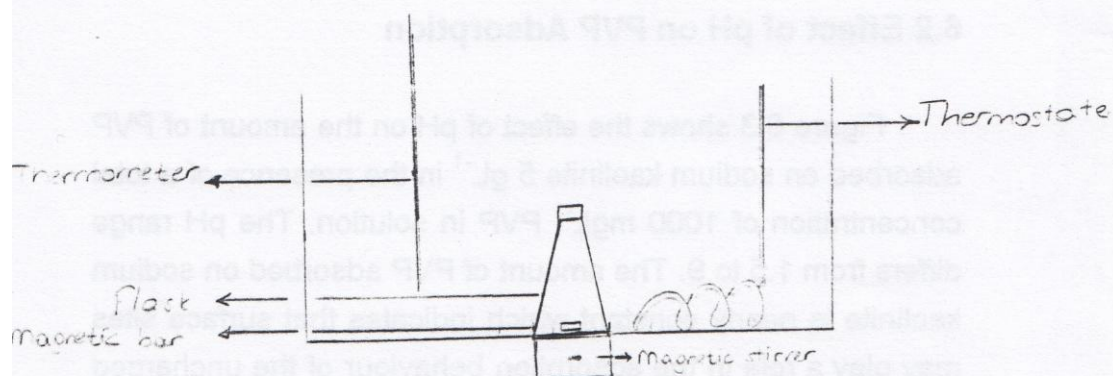


Figure 5.1 The arrangement of the experiment.

6. RESULTS AND DISCUSSION

6.1 Calibration Curve of PVP

The absorption spectrum of polyvinylpyrrolidone with two different molecular weight (K 30 and K 80-100) appears in the ultraviolet region and gives a maximum at 271 nm. The standard solutions were prepared at 0-300 ppm concentration range with both PVP. The calibration curves were convenient with Lambert - Beer law. The calibration curves are shown in figure 6.1 and figure 6.2.

6.2 Effect of pH on PVP Adsorption

Figure 6.3 shows the effect of pH on the amount of PVP adsorbed on sodium kaolinite 5 gL^{-1} in the presence of a total concentration of 1000 mgL^{-1} PVP in solution. The pH range differs from 1.5 to 9. The amount of PVP adsorbed on sodium kaolinite is nearly constant which indicates that surface sites may play a role in the adsorption behaviour of the uncharged polymer (Hild et al., 1997).

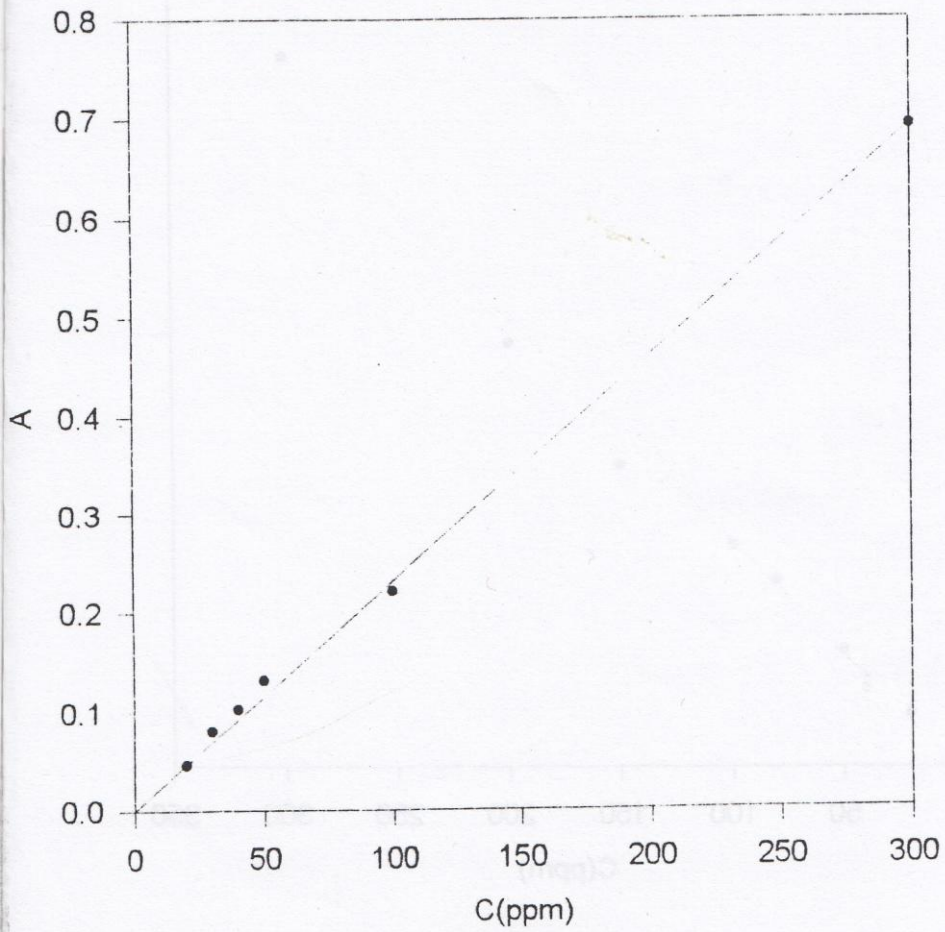


Figure 6.1 Calibration curve of PVP (K 30).

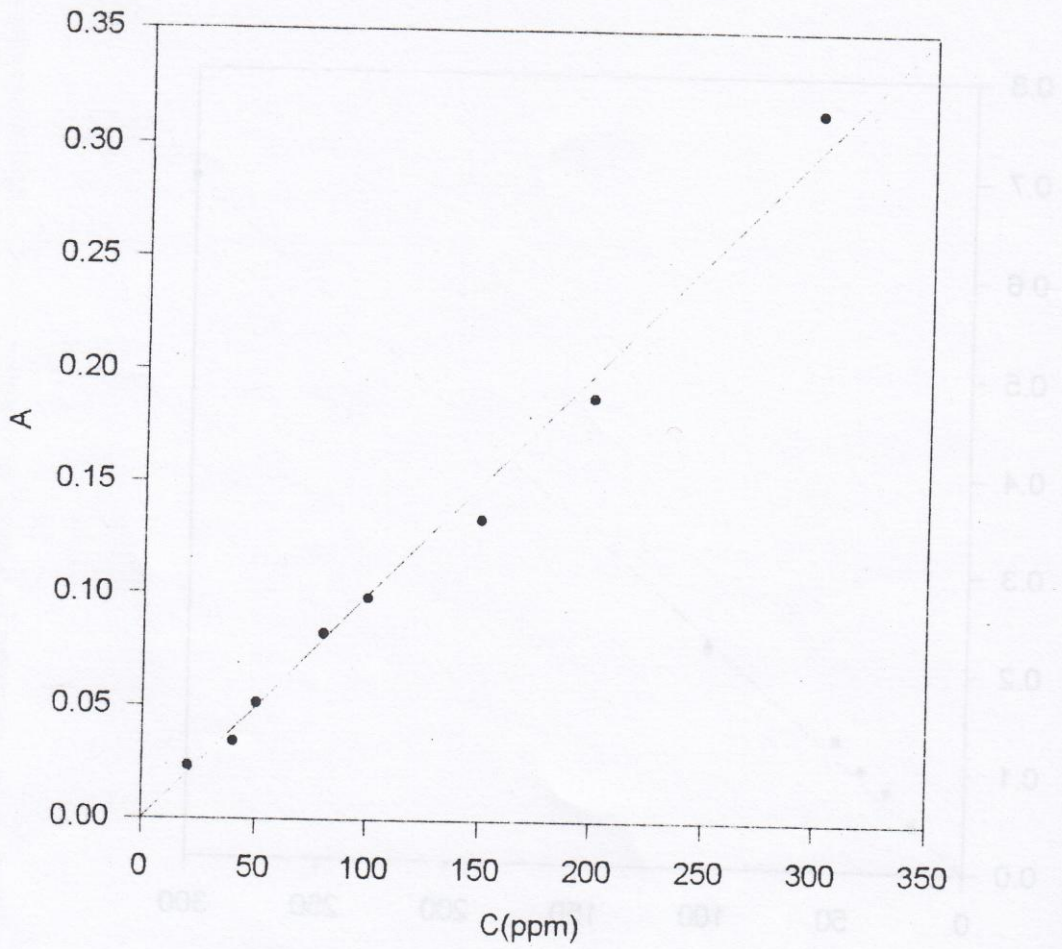


Figure 6.2 Calibration curve of PVP (K 80 -100).

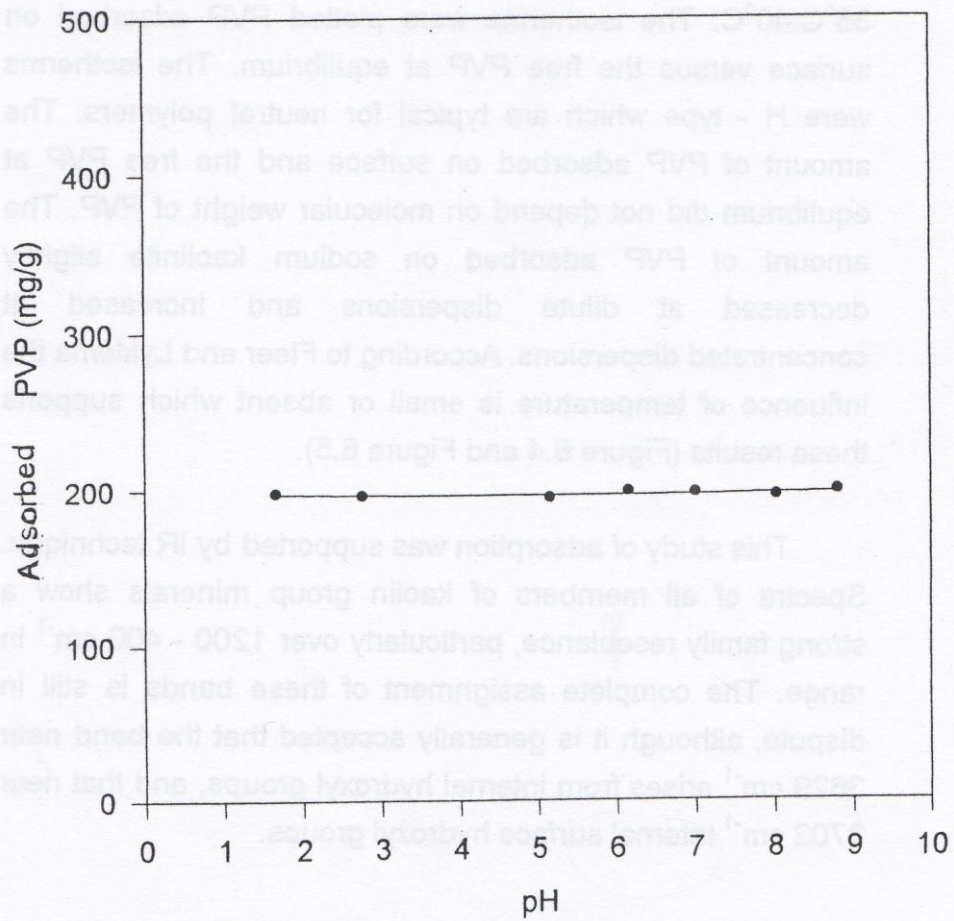


Figure 6.3 Effect of pH on PVP adsorption of sodium kaolinite.

6.3 Adsorption of PVP on Sodium Kaolinite

PVP with two different molecular weight has been adsorbed on sodium kaolinite at 20°C, 25°C, 30°C, 35°C, 40°C. The isotherms were plotted PVP adsorbed on surface versus the free PVP at equilibrium. The isotherms were H - type which are typical for neutral polymers. The amount of PVP adsorbed on surface and the free PVP at equilibrium did not depend on molecular weight of PVP. The amount of PVP adsorbed on sodium kaolinite slightly decreased at dilute dispersions and increased at concentrated dispersions. According to Fleer and Lyklema the influence of temperature is small or absent which supports these results (Figure 6.4 and Figure 6.5).

This study of adsorption was supported by IR technique. Spectra of all members of kaolin group minerals show a strong family resemblance, particularly over 1200 - 400 cm^{-1} in range. The complete assignment of these bands is still in dispute, although it is generally accepted that the band near 3629 cm^{-1} arises from internal hydroxyl groups, and that near 3702 cm^{-1} internal surface hydroxyl groups.

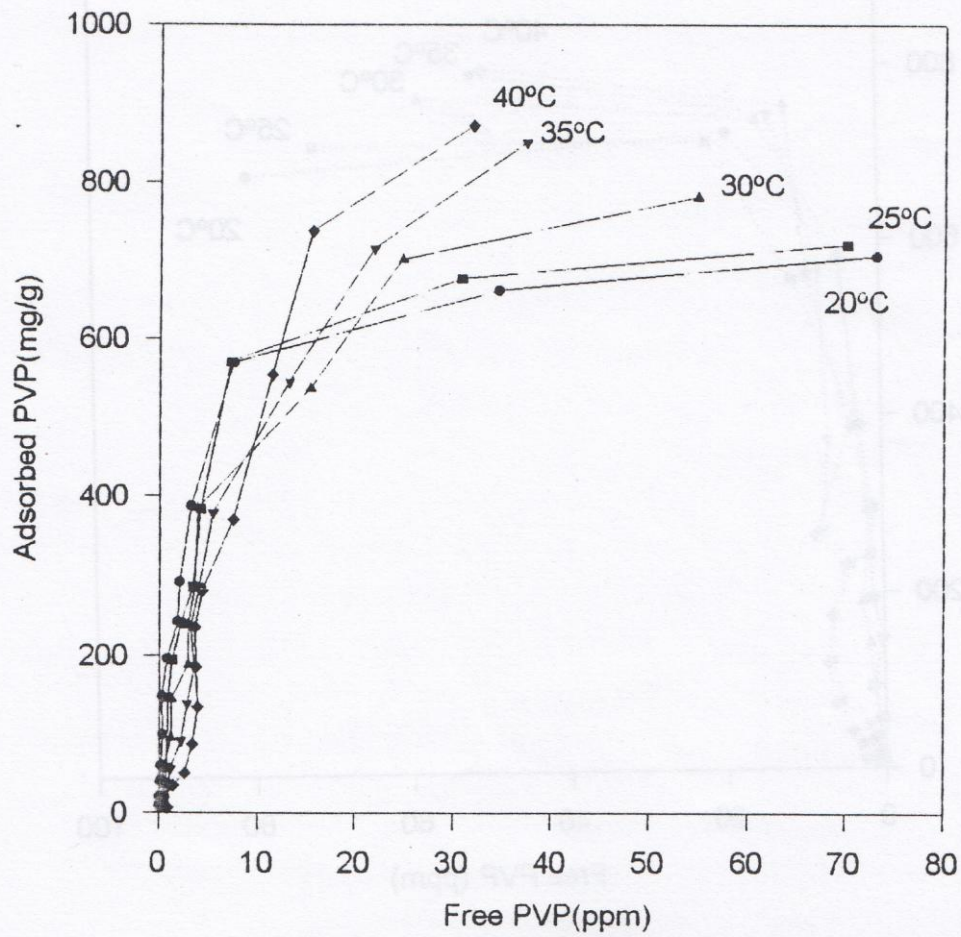


Figure 6.4 Adsorption of PVP (K 30) on sodium kaolinite at different temperatures.

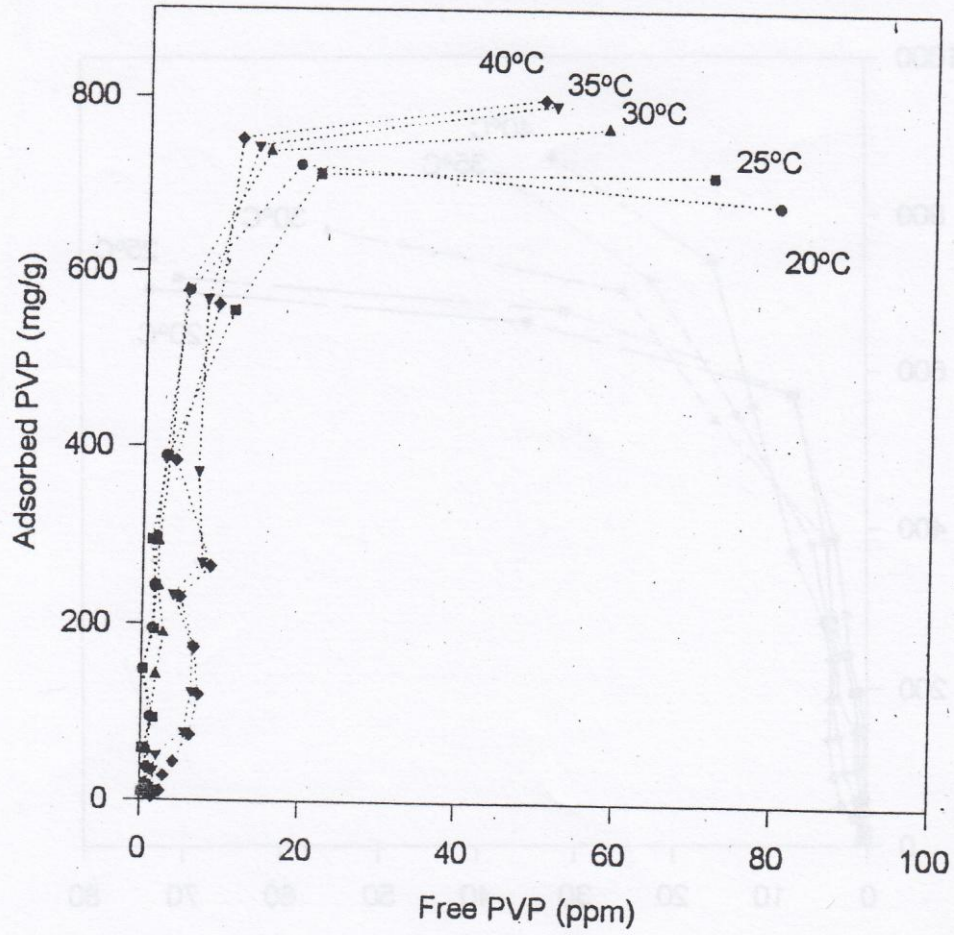


Figure 6.5 Adsorption of PVP (K 80-100) on sodium kaolinite at different temperatures.

Disorder in kaolinite is detectable mainly in the hydroxyl stretching region, although some general broadening of all bands in the spectrum may also occur. While 3629 and 3702 cm^{-1} bands are unchanged, 3672 and 3652 cm^{-1} doublet is replaced by a single broad band at 3656 cm^{-1} . Kaolinite used in this study was a disordered kaolinite (Figure 6.6). The reason of being disordered could arise from the small amount of dickite and / or nacrite-like stacking in the kaolinite (Kodoma and Oinuma, 1963; from Wilson, 1987).

The hydroxyl deformation band of kaolinite at 920 cm^{-1} is typical for the kaolin group, arises from vibrations of the inner surface hydroxyl groups (Wilson, 1987).

After adsorption of PVP (Figure 6.7), the IR spectrum of sodium kaolinite showed two bands at 2952 and 2891 cm^{-1} which were CH_2 - ring stretching modes different from the spectrum illustrated in figure 6.6. The bands at 1550 and 1300 cm^{-1} were CH_2 - scissoring interacted with skeletal modes. The band intensity at 1660 cm^{-1} increased because of the carbonyl group of the PVP.

According to X - ray pattern $d(001)$ distance increased a little which showed that PVP adsorption on sodium kaolinite was mainly on the surface.

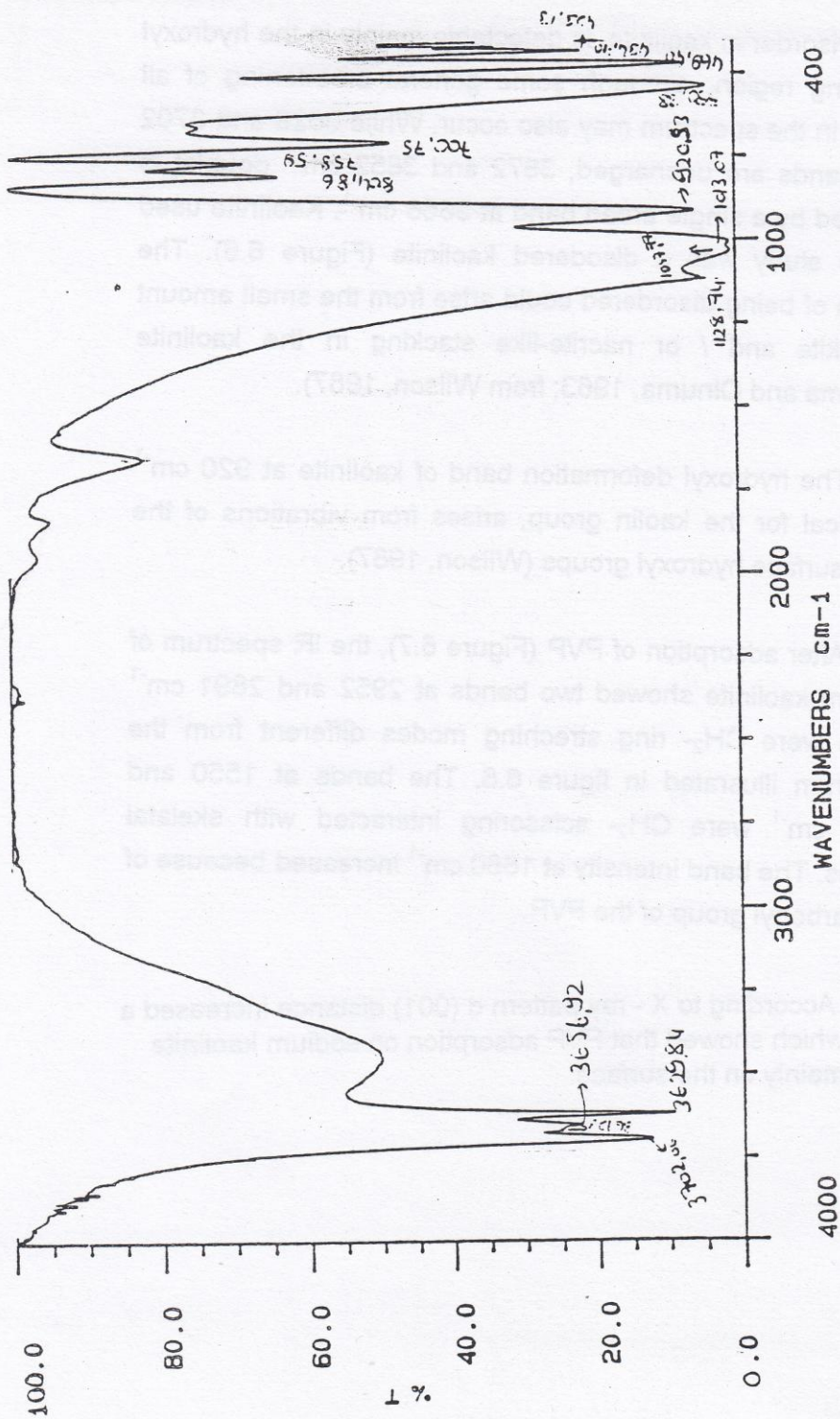


Figure 6.6 IR spectrum of sodium kaolinite before adsorption of PVP.

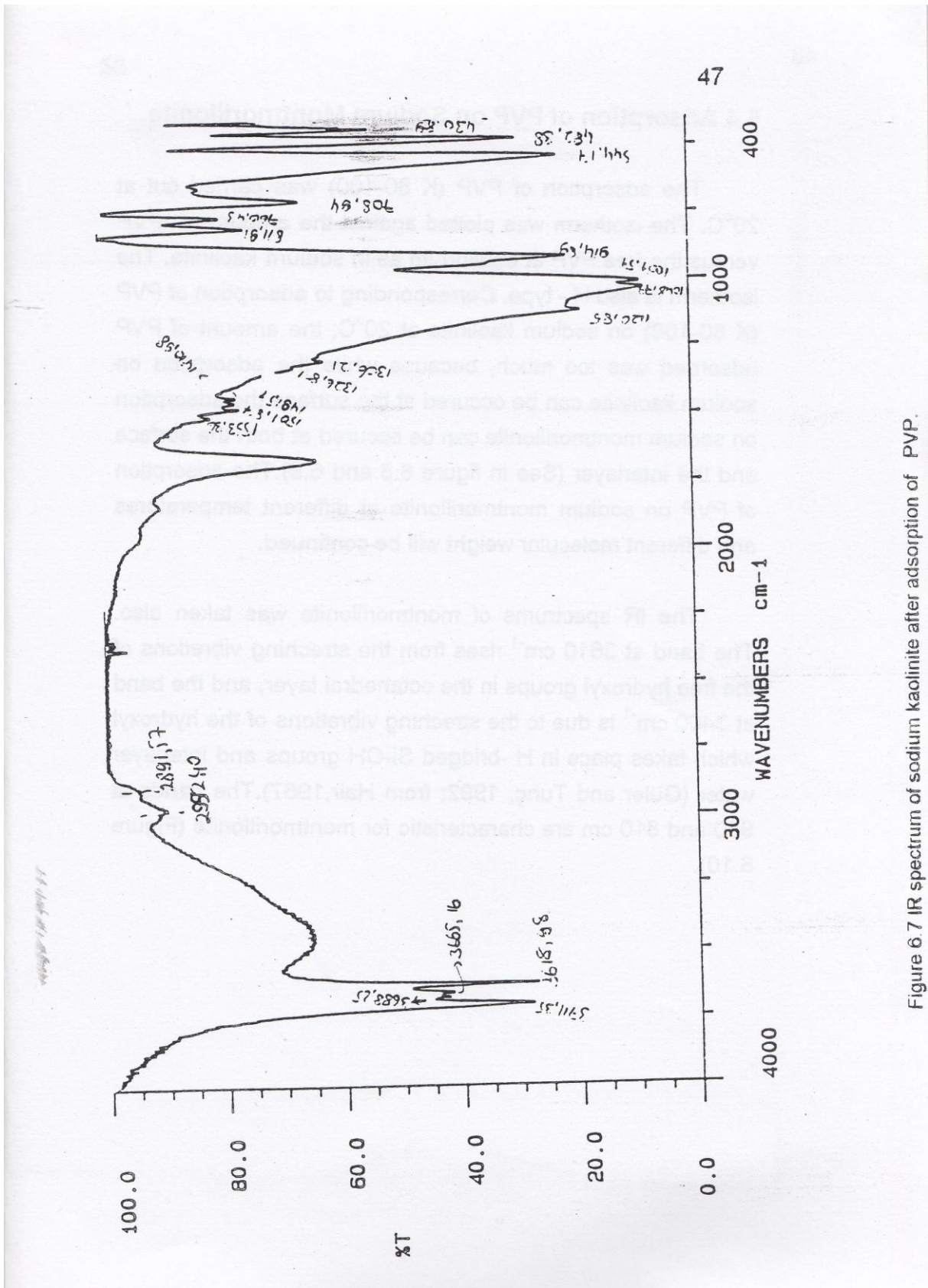
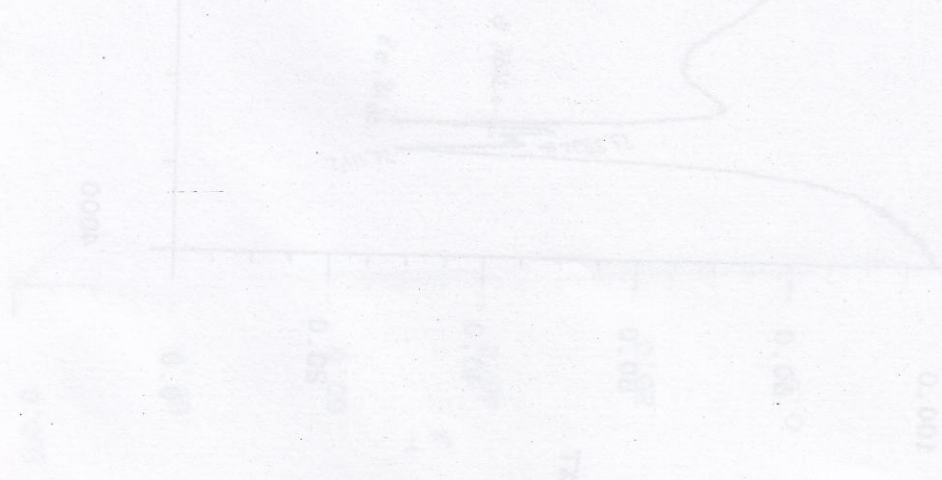


Figure 6.7 IR spectrum of sodium kaolinite after adsorption of PVP.

6.4 Adsorption of PVP on Sodium Montmorillonite

The adsorption of PVP (K 80-100) was carried out at 20°C. The isotherm was plotted against the amount of PVP versus the free PVP at equilibrium as in sodium kaolinite. The isotherm is also H - type. Corresponding to adsorption of PVP (K 80-100) on sodium kaolinite at 20°C; the amount of PVP adsorbed was too much, because while the adsorption on sodium kaolinite can be occurred at the surface the adsorption on sodium montmorillonite can be occurred at both the surface and the interlayer (See in figure 6.8 and 6.9). The adsorption of PVP on sodium montmorillonite at different temperatures and different molecular weight will be continued.

The IR spectrums of montmorillonite was taken also. The band at 3610 cm^{-1} rises from the stretching vibrations of the free hydroxyl groups in the octahedral layer, and the band at 3400 cm^{-1} is due to the stretching vibrations of the hydroxyl which takes place in H - bridged Si-OH groups and interlayer water (Güler and Tunç, 1992; from Hair, 1967). The bands at 980 and 810 cm^{-1} are characteristic for montmorillonite (Figure 6.10).



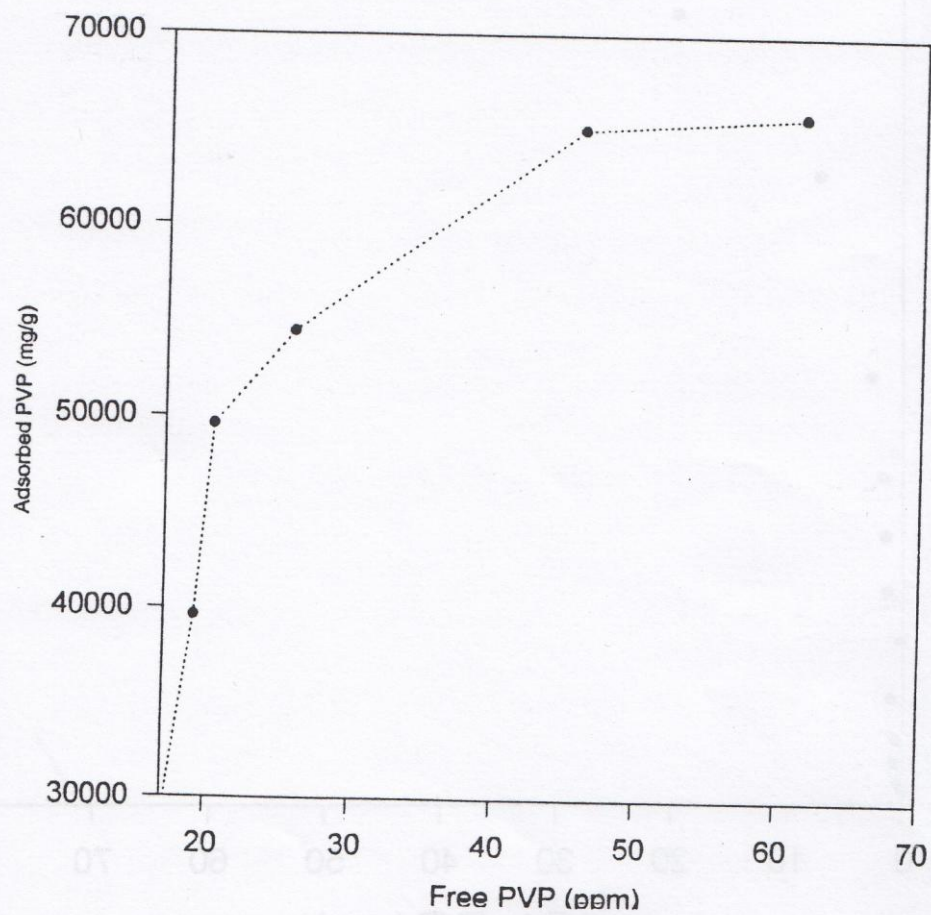


Figure 6.9 Adsorption of PVP (K 80-100) on sodium montmorillonite at 20°C.

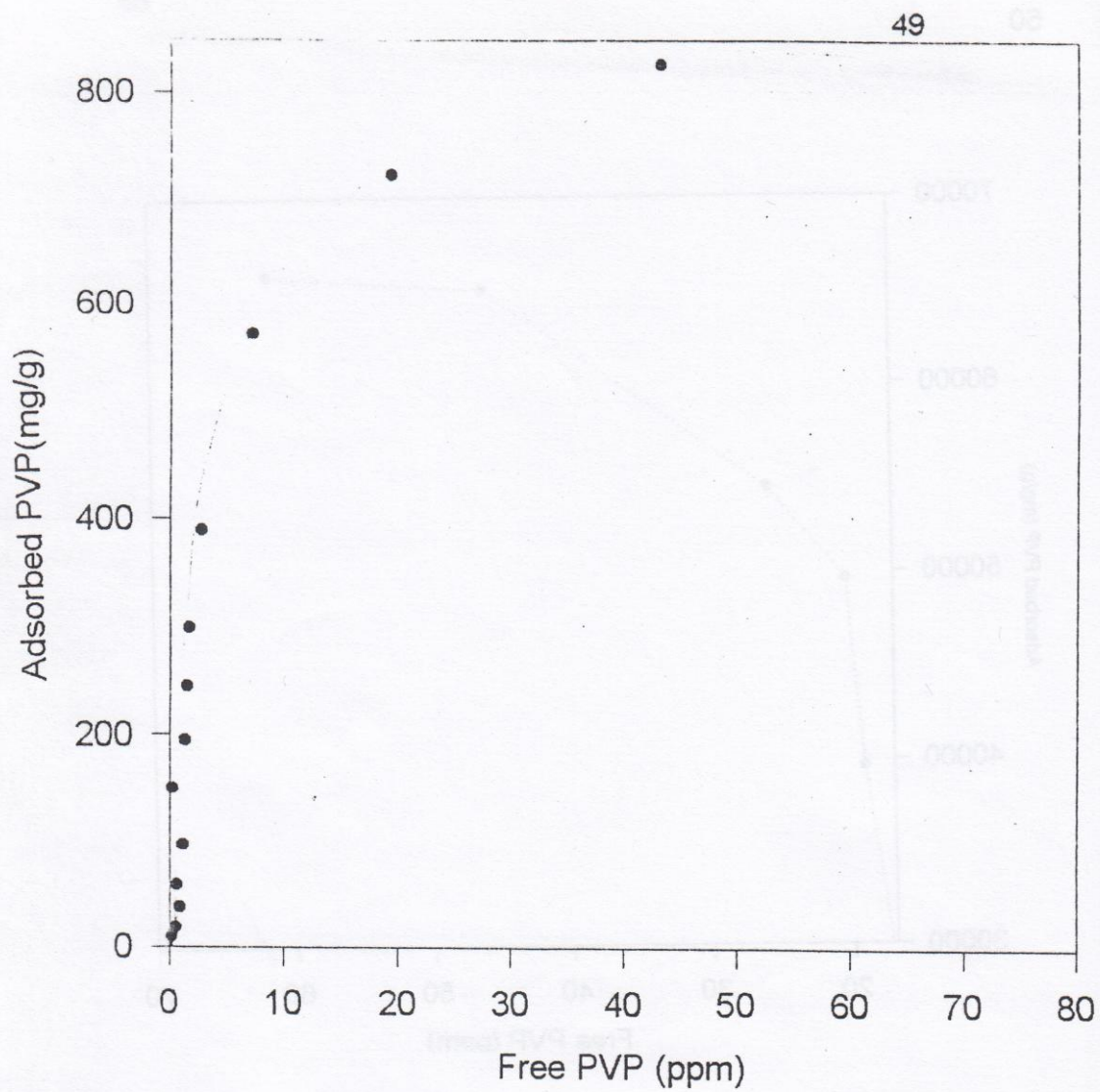


Figure 6.8 Adsorption of PVP (K 80-100) on sodium kaolinite at 20°C.

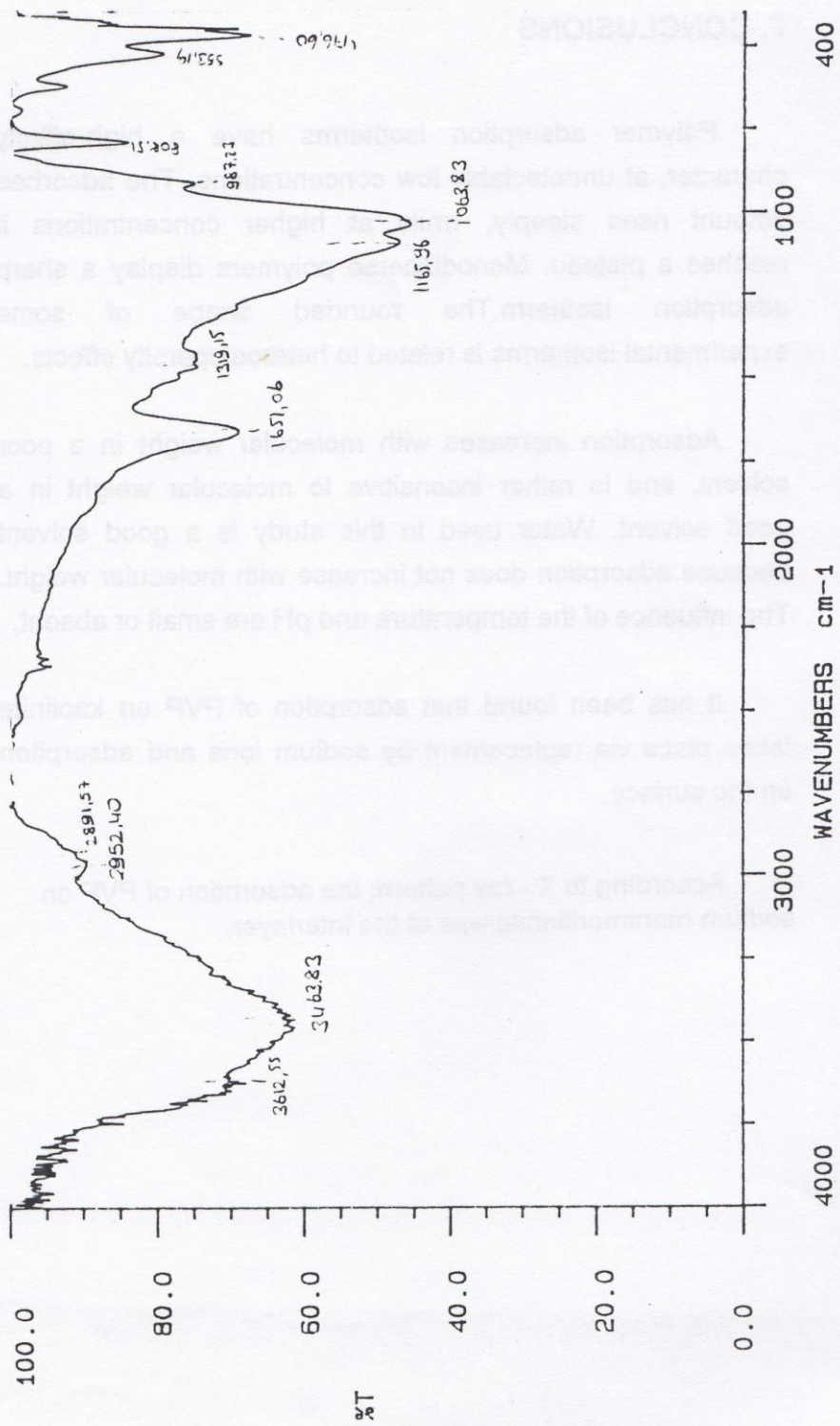


Figure 6.11 IR spectrum of sodium montmorillonite after

7. CONCLUSIONS

Polymer adsorption isotherms have a high-affinity character, at undetectably low concentrations, The adsorbed amount rises steeply, while at higher concentrations it reaches a plateau. Monodisperse polymers display a sharp adsorption isotherm. The rounded shape of some experimental isotherms is related to heterodispersity effects.

Adsorption increases with molecular weight in a poor solvent, and is rather insensitive to molecular weight in a good solvent. Water used in this study is a good solvent because adsorption does not increase with molecular weight. The influence of the temperature and pH are small or absent.

It has been found that adsorption of PVP on kaolinite takes place via replacement by sodium ions and adsorption on the surface.

According to X - ray pattern, the adsorption of PVP on sodium montmorillonite was at the interlayer.

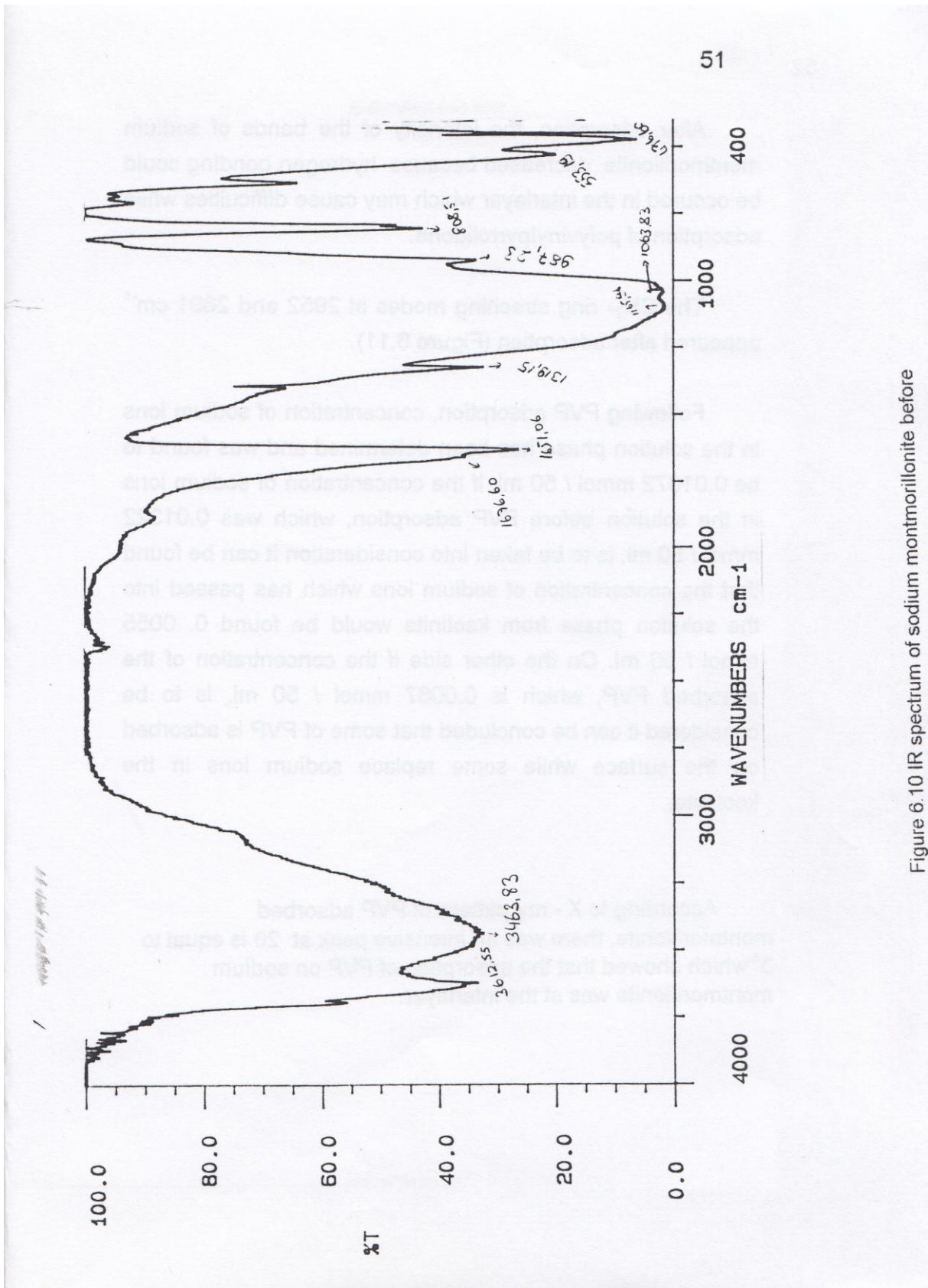


Figure 6.10 IR spectrum of sodium montmorillonite before

After adsorption, the intensity of the bands of sodium montmorillonite decreased because hydrogen bonding could be occurred in the interlayer which may cause difficulties while adsorption of polyvinylpyrrolidone.

The CH_2 - ring stretching modes at 2952 and 2891 cm^{-1} appeared after adsorption (Figure 6.11).

Following PVP adsorption, concentration of sodium ions in the solution phase has been determined and was found to be $0,01872\text{ mmol} / 50\text{ ml}$. If the concentration of sodium ions in the solution before PVP adsorption, which was $0.01322\text{ mmol} / 50\text{ ml}$, is to be taken into consideration it can be found that the concentration of sodium ions which has passed into the solution phase from kaolinite would be found $0.0055\text{ mmol} / 50\text{ ml}$. On the other side if the concentration of the adsorbed PVP, which is $0.0067\text{ mmol} / 50\text{ ml}$, is to be considered it can be concluded that some of PVP is adsorbed on the surface while some replace sodium ions in the kaolinite.

According to X - ray pattern of PVP adsorbed montmorillonite, there was an intensive peak at 2θ is equal to 3° which showed that the adsorption of PVP on sodium montmorillonite was at the interlayer.

REFERENCES

- Berner, R.A., 1971, Principles of Chemical Sedimentology, McGraw-Hill Book Com., New York, 240p.
- Fleer, G.J. and Lyklema J., 1983, Adsorption of Polymers, 153-156, Adsorption from Solution at the Solid / Liquid Interface, Parfitt G.D. and Rochester C.H. (Eds), Academic Press Inc., London, 416 p.
- Francis, C.W., 1973, Adsorption of polyvinylpyrrolidone on reference clay minerals, *Soil Science*, 115(1): 40-54 pp.
- Fripat, J.J., Jelli, A., Poncelet, G. and Andre, J., 1965, Thermodynamic properties of adsorbed water molecules and electrical conduction in montmorillonites and silica, *Journal of Physical Chemistry*, 69 : 2185-2197pp.
- Greenland, D.J., 1965, Soils and Fertilizers, Wiley Ltd., New York, 415p.
- Grim, R.E., 1968, Clay Minerology, McGraw-Hill Com., New York, 596p.
- Güler, Ç., Tunç, F., 1992, Chlorophyll adsorption on acid-activated clay, *Jaocs*, 69(9): 948-950 pp.
- Hair, M.L., 1967, Infrared Spectroscopy in Surface Chemistry, Marcel Dekker Inc., New York, 315p.
- Hall, P.L., 1987, Clays: their significance, properties, origins, and uses, 1-23, A Handbook of Determinative Methods in Clay Minerology, Wilson, M.J. (Ed.) , Blackie and Son Ltd., London, 308p.

- Hild, A., Sequaris, J.M., Narres, H.D., Schwuger, M., 1997, Adsorption of polyvinylpyrrolidone on sodium kaolinite, *Colloids and Surfaces A : Physicochemical and Engineering Aspects*, 123-124: 515-522 pp.
- Lipatov, Y.S., 1974, Adsorption of Polymers, Wiley Ltd., New York, 254 p.
- Napper D.H., 1983, Colloid Science Monograph, Academic Press, London, 345 p.
- Newman, A.C.D., 1984, The significance of clays in agriculture and soils, *Philos. Trans. Roy. Soc.*, London, A 311: 375-389 pp.
- Schofield, R.K., 1953, The defoccculation of kaolinite suspensions and the accompanying changeover from positive to negative chloride adsorption, *Clay Minerals Bulletin*, 2: 45-51 pp.
- Somasunduran, P., 1997, Adsorption of surfactants and polymers at the solid-liquid interface, *Colloids and Surfaces A: Physicochemical Aspects*, 123-124: 491-513 pp.
- Swartzen-Allen, S.L., 1974, Surface and colloid chemistry of clays, *Chem. Rev.*, 74: 385-400 pp.
- Theng, B.K.G., 1979, Formation and Properties of Clay-Polymer Complexes, Elsevier Scientific Publishing Com., New York, 362 p.

Van Olphen, H., 1977, An Introduction to Clay Colloid Chemistry, Wiley Ltd., New York, 318 p.

Private Address
 1434 str. No. 214
 Alsancak / Izmir
 Phone : 02324215233

Personal
 B. Sc. Univ. Izmir
 Ege University
 Chemistry Department of
 Science Faculty
 (Physical Chemistry)
 35100 Bornova, Izmir / Turkey
 Phone : 02323880110 / 2393

Citizenship : T.R.
 Date of Birth : 28 / 09 / 1974
 Marital Status : Married
 Place of Birth : Izmir / Turkey

Academic Background or Degree Obtained:

<u>Period</u>	<u>Academic Status</u>	<u>Department</u>	<u>University</u>
1997-98	B. Sc.	Chemistry	Ege Uni.
1995-98	M.Sc.	Chemistry (Physical Chemistry)	Ege Uni.

Class rank : Fourth Place
 Grade average : 78.00

CURRICULUM VITAE

Personal

B.Sc. Lina Israel
Ege University
Chemistry Department of
Science Faculty
(Physical Chemistry)
35100 Bornova, Izmir / Turkey
Phone : 02323880110 / 2393

Private Address

1434 str. No: 2/14
Alsancak / Izmir
Phone : 02324215720

Citizenship : T.R

Date of Birth : 28 / 09 / 1974

Martial Status: Married

Place of Birth : Izmir / Turkey

Academic Background or Degree Obtained:

<u>Period</u>	<u>Academic Status</u>	<u>Department</u>	<u>University</u>
1992-96	* B. Sc.	Chemistry	Ege Uni.
1996-99	M.Sc.	Chemistry (Physical Chemistry)	Ege Uni.

* Grade average : 76.00

Class rank : Fourth Place