CHAPTER : 1

INTRODUCTION

INTRODUCTION

Macromolecules are ubiquitous. Their existence is taken for granted in food, clothing, shelter, transportation, communication and various other aspects of modern technology. It is surprising that just 50 years ago, Herman Staudinger was given the advice **"Dear Colleague, Leave the concept of large molecules well alone ..... there can be no such thing as a macromolecule"**. However, since Goodyear's discovery of vulcanization of rubber in 1839, Hyatt's invention of plasticized cellulose nitrate in 1870, Chardonnet's manufacture of a man-made fibre in 1884, and Baeckeland's synthesis of phenolic resins in 1909, the pace of polymer science and technology has been accelerating dramatically. As a class, polymers are among the most important of all materials. They are infact the basis of life itself; among the many constituents of living organisms, proteins perform a great variety of functions in both animal and plant kingdoms; more complicated polymers determine hereditary characteristics and control the biological development; starch is a vital part of our diet; cellulose is the main structural material of plants; natural rubbers and natural resins have their specific functions and so on. Synthetic polymers, almost unknown fifty years ago, are now made and processed in plastics, synthetic rubber and man-made fibre industries.

The applications of polymers are legion and in many applications, their surface characteristics, inter alia, are of great concern and of importance. One of the most important fields of the physical chemistry of polymers and colloid chemistry is the physical chemistry of surfaces. The study of polymer surfaces is important from both fundamental and applied points of view. This is because the creation of new polymeric materials, from polymers used in everyday life to those employed in space engineering, involves the application of heterogeneous polymeric systems. It is clear that most polymeric materials are heterogeneous systems, with highly developed interfacial areas.

These polymers include reinforced plastics, filled thermoplastics, reinforced rubber, lacquer - varnish coatings, glues and others. Thus, a study of the behaviour of macromolecules on the interface is one of the most important tasks in the field. The problem of surface phenomena in polymers has many aspects. It includes questions such as the adhesion of polymers to solid surfaces, the structure and properties of monolayers, the structural and mechanical properties of the boundary layers of polymers in contact with solid bodies, etc. However, all these questions are closely related to a central problem, namely, the adsorption of polymers on solid surfaces.

1.1 WHAT IS ADSORPTION ?

When two different phases come in contact with each other, then there is a possibility of sorption of one phase on another. The sorption involves two different processes i.e. the adsorption and the absorption. To define adsorption, we can say that when two phases, atleast one of which is liquid or gaseous, come into contact with each other, the composition of these phases close to the phase boundary will differ from the composition observed in regions distant from that boundary [interface] i.e. within the bulk. This phenomenon of increase in concentration in the interfacial region where the phases are in mutual contact, relative to the concentration in the bulk, is called adsorption /1/. Adsorption may be either due to preponderance of physical or chemical forces and the phenomenon is called physisorption or chemisorption respectively. In physisorption, the electron cloud of the adsorbate interacts as a whole with the adsorbent, resulting in the polarisation of the adosrbate molecules. In chemisorption, on the other hand, electron transfer and sharing of electrons [formation of a new molecular orbital] takes place between the adsorbate and the adsorbent, as in the case of chemical compounds. The magnitude of the energy change in the former case is much smaller than the latter one /2/. As to the mechanism of the process of adsorption of gases, it was in the beginning generally accepted that the gas molecules were attracted towards the surface of the solid adsorbent due to physical forces only. The difference between chemisorption and chemical compound is that in the former case, inspite of the electron sharing with the adsorbate molecules, the surface atoms of the adsorbent remain simultaneously bonded with other atoms in the bulk /3/.

1.2 APPLICATIONS

The process of adsorption is encountered in varied fields of technology and chemical analysis. Innumerable industrial processes, starting from the synthesis of ammonia to the manufacture of alcohol or synthetic petrol, are heterogeneously catalysed reactions /4/. Most of these catalysed reactions are effected through adsorption of reactants on solid surfaces. Among other industrial applications, adsorption plays an important role in the field of drying /4/. On an industrial scale, adsorption equipment is used, for example, to dry hydrocarbons, alcohols, hydroxy and chloro derivatives of hydrocarbons, permanent and rare gases /5/. Another important application of adsorption in industry is in recovering industrial solvents. Adsorption processes are continuously increasing importance in connection with air and water purification. The function of gas masks is based upon preferential adsorption of harmful gases present in the atmosphere by the use of suitable adsorbents in order to purify the air for inhalation /6/. The role of charcoal in the recovery of iodine and many dyes from their dilute solutions, or its role in the clarification of syrups in sugar industry, are based on its adsorption capacity. Chromatographic methods, which are widely used nowadays in separating and analysing valuable and minute quantities of components from a mixture, are also based on adsorption. The successful separation of rare earth elements by chromatographic method using fractional adsorption on organic resins is an outstanding example /6/.

The adsorption of macromolecules on surface is a phenomenon of both, academic and technological interest /7-10/. The several facets of polymer adsorption have been adequately summarized in many recent reviews /11-18/. The use of adsorbed macromolecules to stabilize colloidal dispersions, e.g. pharmaceuticals, dyestuffs, inks, and paints has a long history and has been intensively studied over the past few decades /19-22/. The technological importance of colloid stabilization and destabilization by polymers has resulted in extensive experimental and theoretical studies of polymer adsorption /23,24/. An example of such a destabilization process is waste water treatment. Polymeric flocculants are now an essential part of sludge processing operations, such as thickening and dewatering [water removal from a suspension to form a slurry or cake] /25/. Adsorption of polymers is also involved in other processes, including corrosion control, detergency, lubrication, drag reduction, film deposition, soil phenomena, tertiary oil recovery, biomembranes and membrane separations /26/. The interfacial properties of dilute polymer solutions are of fundamental importance in diverse fields such as foaming, coating, printing flows, porous media flows, chromatography and hydrodynamic lubrication /27/. The formation of glued joints, the application of varnish-lacquer coatings include adsorption of polymers on the surface as the first stage. Besides this, adsorption of macromolecules plays an important role in various biological and industrial applications, including space engineering /28/. Surface phenomena are also important in application of polymers to medicine, biochemistry, bioengineering, and immunochemistry /29/.

Great strides have been made in adhesion science. Adhesional interaction between the polymer-solid interface is mainly adsorptional in nature /30/. The properties of any composite will depend to a large extent on adhesion between the components. The interaction of macromolecules with the filler leads to the formation of adsorption layers, which determine to a considerable extent, many properties of polymer-filler composites /31/.

The interaction of polymeric materials with solids appreciably changes all the properties of polymers, as the adsorptional interaction reduces the molecular mobility of the chains during moulding operation. The state in which two surfaces are held together by interfacial forces may consist of valence forces, diffusion or interlocking action. The bonding of various rubbers with the various additives and reinforcing fillers is a primary requirement for engineering end uses and many composite products like tyres, belting, hoses, etc. These reinforcing and/or cost reducing fillers are exclusively used in the rubber products like tyres, tubes, gaskets etc. and also in many other high performance plastics like reinforced plastics, thermosetts, composites and many others.

1.3 RUBBERS, FILLERS, AND REINFORCEMENT

Fillers have played an important role in the rubber and plastic industries. In fact, the early growth of the phenolic plastic industry would not have been possible without the enhancement of the required properties by the use of fillers /32/. The same applies for rubber industries too. Rubber material is seldom, if ever, used in the original form. The manufacture of articles from rubber involves the addition of many other materials to the raw rubber. As soon as Thomas Hancock discovered that the mechanical working softened natural rubber, a process called mastication, the mixing of other materials with it was possible; the ability of the raw rubber to absorb susbstantial quantities of mineral fillers e.g. oxides of silica in powder form was no doubt soon apparent. In rubber technology, the term reinforcement is often used without any reservation to any particular improvement in the properties of rubber. It is taken to imply "the incorporation into rubber of substances having small particles, which give to the vulcanisate high abrasion resistance, high tear, tensile strength, and an increase in stiffness" /33/. Rubber technologists believe that colloidal carbon is the best example of a truly reinforcing filler; and basic studies of reinforcement have been mainly concerned with this material /33/. The last decade has seen the development of fine silica, capable of producing a high degree of reinforcement /34/. In 1939 reinforcing silica fillers were first introduced and by 1949 precipitated silicas [containing 85-90% SiO_2] and pyrogenic silicas [containing 99.8% SiO_2] were discovered. Precipitated silicas are excellent non-black reinforcing fillers for rubbers. They impart exceptional cut and chip resistance, when used in off-the-road tires for heavy construction equipment /35/. Precipitated silicas [30 to 90 phr] are generally used for high grade shoe soles and heels to achieve stiffness, abrasion resistance, flex resistance and nonmarking features. In fact, precipitated silicas reinforce, practically every type of rubber : natural, SBR, butyl, neoprene, nitrile and so on /36/. Due to higher cost, pyrogenic silicas are used as reinforcing fillers for high cost compounds e.g. silicone rubber.

Precipitated aluminium hydroxide [hydrated], a white fine powder, is also a reinforcing filler in shoe soling and mechanical goods. It is the fine particles of carbon blacks, silicas, alumina, which act as "reinforcing agents". The larger particles act as valuable fillers for adjustment of hardness and processing characteristics. Mineral silica, or sand, ground below 200 mesh is a cheap filler for heat resistant compounds, but has no effect on cure. Light colour products also use carbon black because it provides a higher degree of reinforcement than precipitated silica /37,38/.

The addition of fillers is almost as old as the use of rubber itself. It was Christopher Columbus, who during his second voyage to the New World in 1496, found the natives of Haiti playing with a ball, made from the gum of a tree - a ball which bounced. In South America, such trees were called "Cau-uchu" or "weeping wood". In fact, games were played with such a rubber ball, as far back as eleventh century. English chemist, Priestley, gave the name "rubber" to the raw material in 1770, on finding that it would "rub off" pencil marks. A London coachman, Thomas Hancock, then cut rubber into long strips and invented rubber band in 1823. In 1839,, the tremendous discovery of vulcanization by Thomas Hancock and Charles Goodyear, ultimately made possible the multibillion dollar rubber industry of today. In 1846, Thomas Hancock made solid rubber tyres for the carriage of Queen Victoria, perhaps thereby launching the present vast tyre industry /39/. So, the discovery of vulcanization, timed with industrial revolution, caused a great demand for raw [natural] rubber. John Dunlop's discovery of tyres in 1887 revolutionized transportation and created a vast demand of natural rubber /40/.

Although polybutadiene rubber was first produced in Europe in early 1930s, it was virtually unknown until 1960 to U.S. rubber industry. The discovery of organometallic catalysts for polymerization of butadiene in hydrocarbon solvents brought a drastic change in the industry.

Polybutadiene rubber [PBR] is being used in almost all tyre and nontyre applications. It is used in tyre treads, in mixtures with other rubbers, to improve abrasion resistance and crack resistance. In carcuss compounds and sidewall stocks, upto about 30% of the rubber used may be polybutadiene, to improve resistance to heat. Nontyre applications take advantage of its abrasion resistance, flexible crack resistance, resilience properties and excellent low temperature flexibility. Thus, from its origin at the beginning of the last century, the rubber industry has evolved into a complex and highly sophisticated technological activity. Natural and synthetic rubbers have become essential to everyday living and have influenced developments in the automobile, communications, aircraft and many other industries.

Adsorption of natural /41/ and synthetic rubbers onto carbon black has been extensively studied in relation to the development of rubber technology /42-48/. From a practical standpoint, as seen before, instead of carbon black, silica and alumina have sometimes been used as reinforcing materials for elastomers /49/. The literature survey did not show a detailed study of the adsorption of natural and synthetic rubbers on silica and alumina, hence the present study was undertaken.

1.4 ADSORPTION ISOTHERMS

[a] Small Molecules

The first empirical relationship, to explain the adsorption of gaseous molecules on solid adsorbents was put forward by Freundlich. The failure of Freundlich isotherm at higher pressures and some other observations indicated that the concept of physical adsorption did not wholly explain the experimental results /1,3/. In 1916, Langmuir introduced a new concept involving chemical forces. According to him, the atoms in the interior of the solid adsorbent have their field of force wholly satisfied by the surrounding atoms /3/. The atoms on the surface are not completely surrounded on all sides, hence these have resultant forces due to those unshared electrons towards the interior.

This leads to sharing of electrons with the adsorbate molecules and a sort of covalent linking is formed between the adsorbent and adsorbate molecules. Langmuir assumed that adsorbate molecules form monomolecular layer on the surface of the adsorbent. This results in the characteristic Langmuir type of isotherm.

Brunauer /50-52/ put forward five principal forms, as shown in Fig.1.1. Out of the five types shown, Type I is the Langmuir type and Type II corresponds to a multilayer formation on the adsorbent. The other three types shown in Fig.1.1 are relatively rare /53,54/. Two additional isotherms have also been reported [Fig.1.2] after

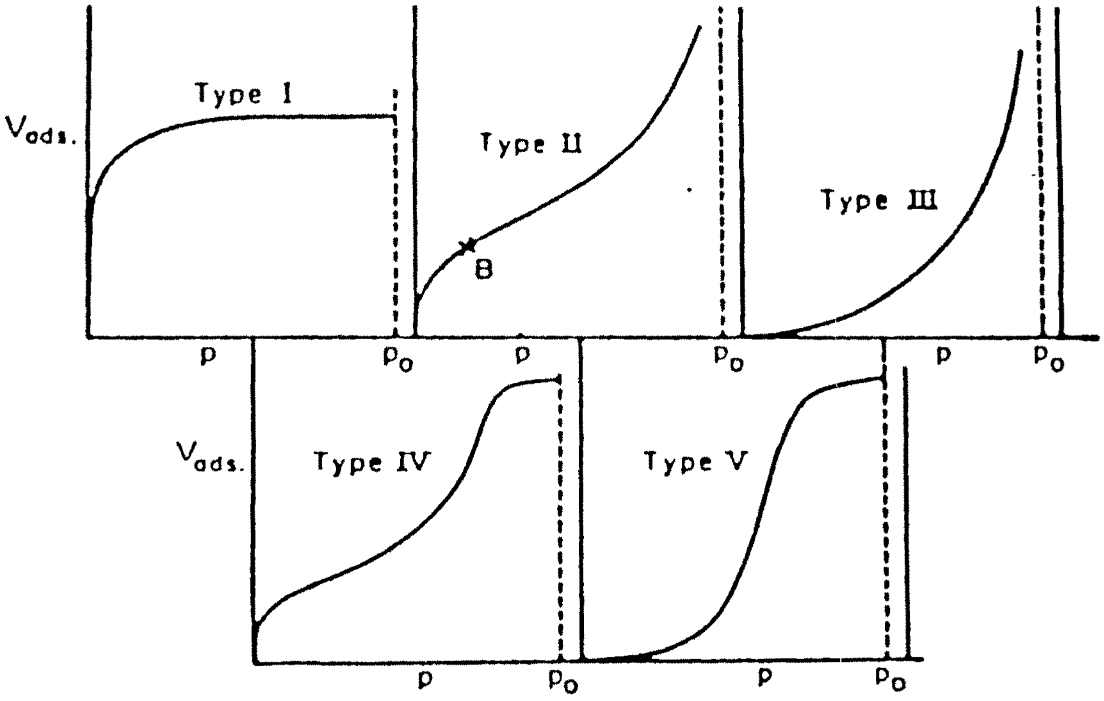
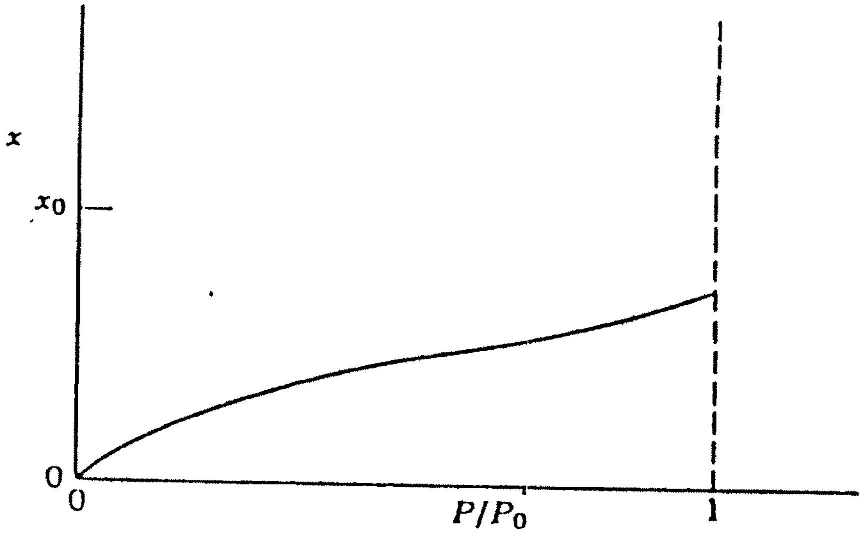
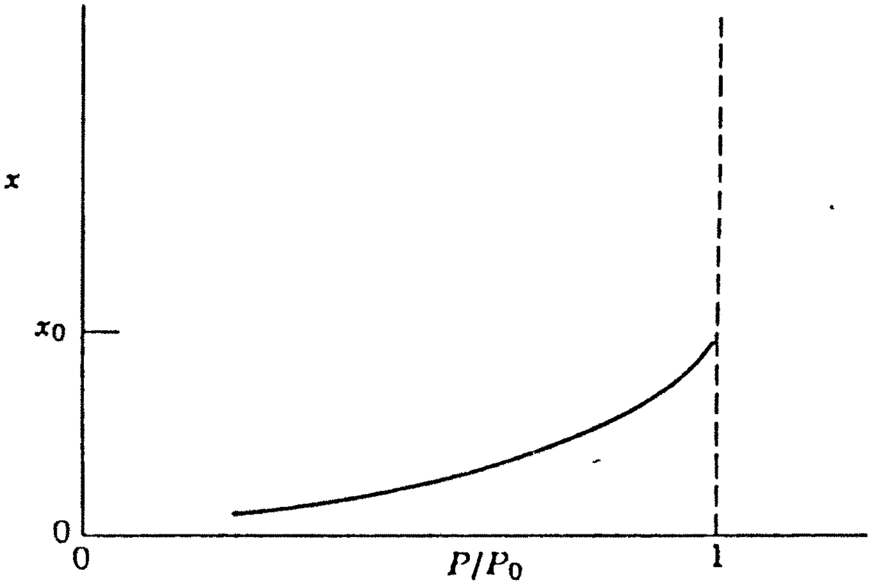


Fig.1.1 Various forms of adsorption isotherms - according to Brunauer.



Type VI

(a)



Type VII

(b)

Fig.1.2 Two additional types of adsorption isotherms

Brunauer's original classification /55,56/. In addition, there are some isotherms which do not fit into Brunauer's classification at all, the most notable being stepwise isotherms, an example is given in Fig.1.3 /57/.

During the first three decades of this century, innumerable investigations were done on adsorption of gases under different circumstances on various solids. Experimentally, the investigation of adsorption from solution is simpler though theoretically more complicated with respect to gas adsorption. The adsorption from solution always involves competition between solute and solvent or between the components of a liquid mixture, for the adsorption sites. Apparent, rather than true isotherms are therefore calculated from changes in solution concentration /58-60/. Various examples of adsorption of small molecules from solutions at different temperatures are available in the literature /61-66/.

The various isotherms obtained for the adsorption from dilute solution have been classified by Giles et al. /64/. The various isotherm shapes recognized are shown in Fig.1.4 /65/. Four characteristic classes are identified, based on the initial part of the isotherm, the subgroups relate to the behaviour at higher concentrations /66/. Giles et al. /67,68/ relate the adsorption mechanism, orientation of adsorbed molecules and orientation changes, etc. to the shape of the isotherm in a detailed theoretical discussion. The Class H isotherms of Fig.1.4 correspond to the adsorption of very large molecules like polymers.

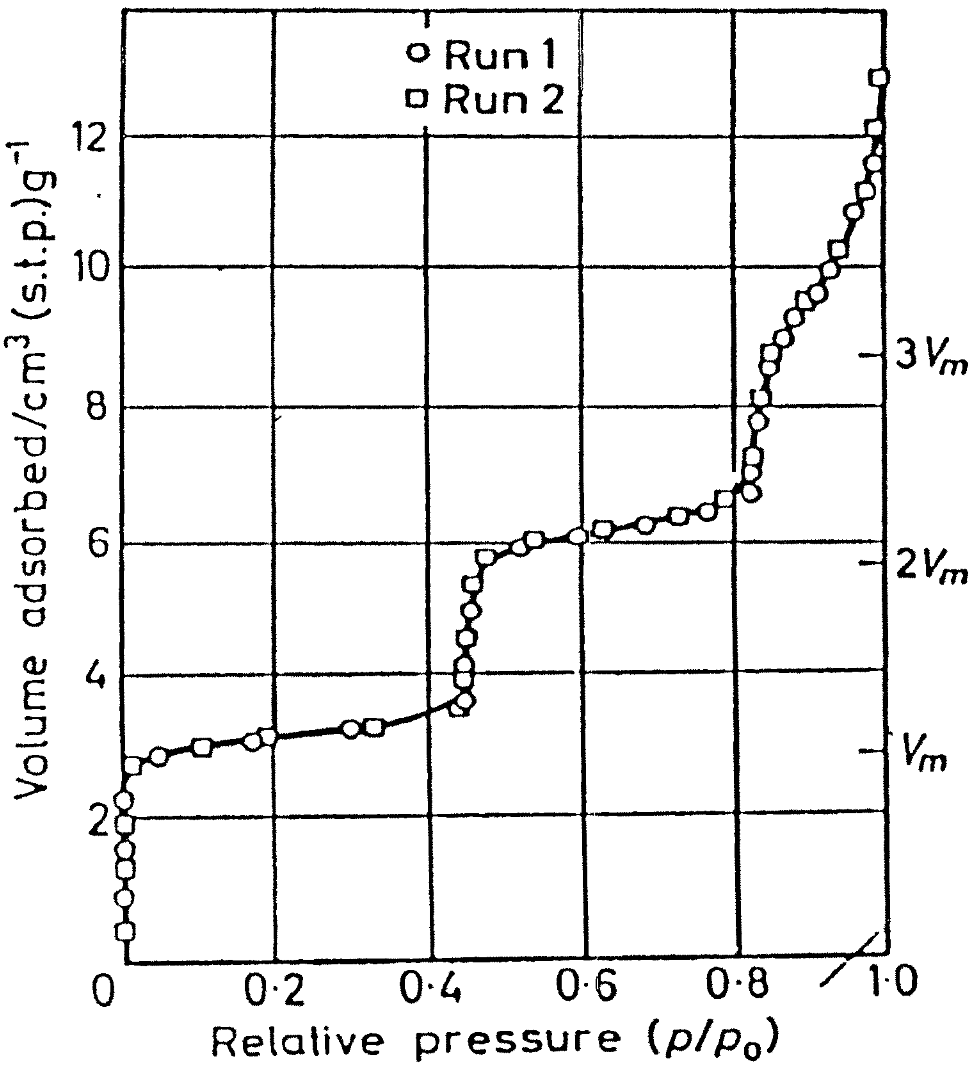


Fig.1.3 Stepwise adsorption isotherm

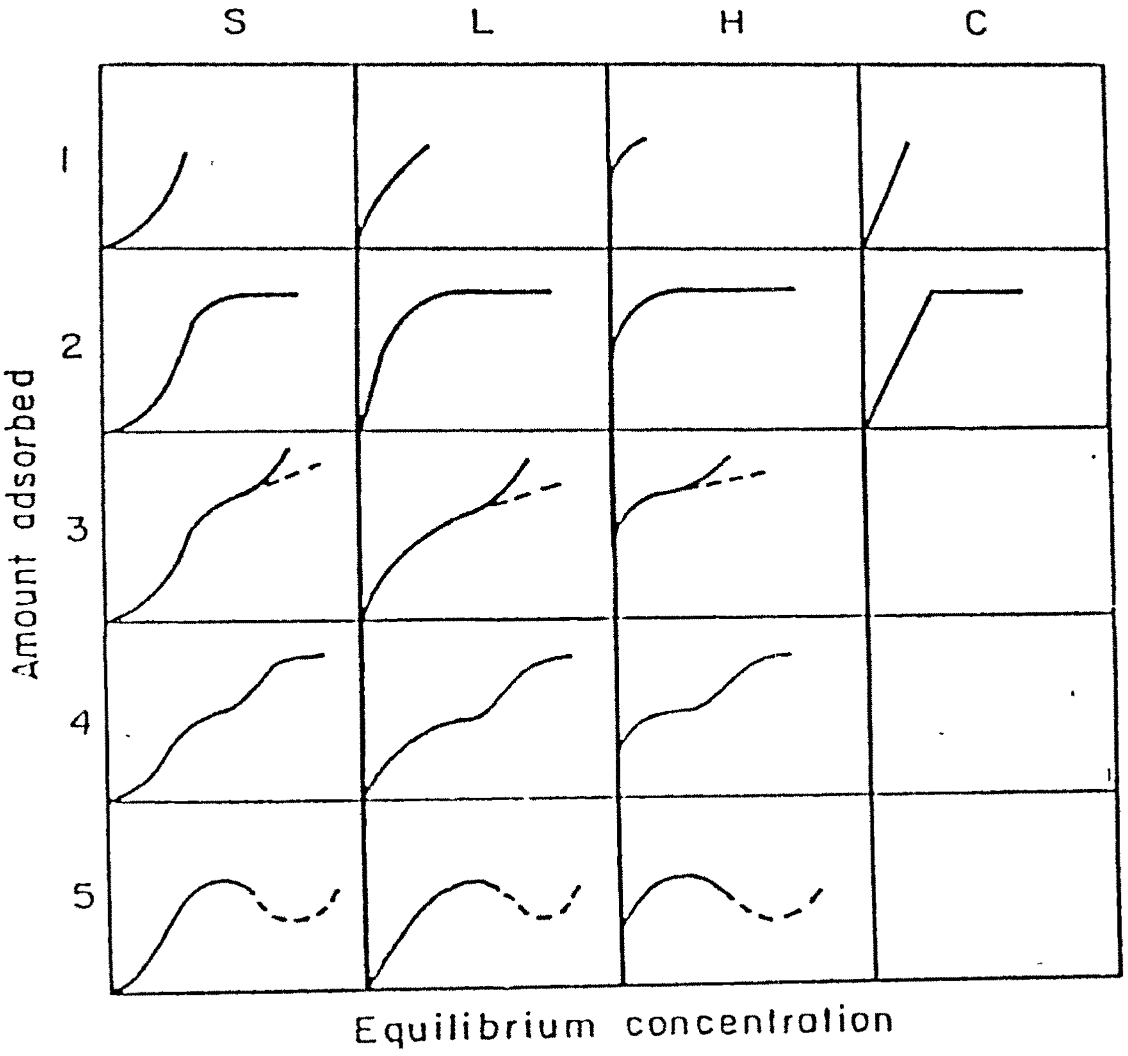


Fig.1.4 Classification of isotherm shapes

[b] Polymer Molecules

The adsorption of polymers at solid-liquid interface differs in many respects from that of small molecules. This difference is mainly due to various configurations that a macromolecule can assume, both in the bulk of a solution and at an interface. In an adsorbed linear macromolecule, three types of segment sequence can be distinguished : trains, loops and tails, shown in Fig.1.5 /69/. This distinction was first proposed by Jenkel and Rumbach /70/ and also supported by others /71/. A train is a series of consecutive segments, all in contact with the surface, a loop consists of segments only in contact with the solvent, and is bound by a train on each side. A tail is terminally bound to a train; the other end dangles in the solution. Depending upon various parameters, such as nature of solvent, molecular weight of polymer, free energy of adsorption per segment, etc. a certain distribution of size of loops, trains and tails generally develops. Therefore, it is possible that adsorbed polymer molecule will possess a great many internal degrees of freedom. These permit the motion of unadsorbed segments to a much greater extent than would be possible for small molecules. Besides this, there are other differences /72/ :

[1] The segments may be "adsorbed" although they are not in direct contact with the surface i.e. in loops or tails rather than trains.

[2] It is difficult to desorb the polymers by dilution [although

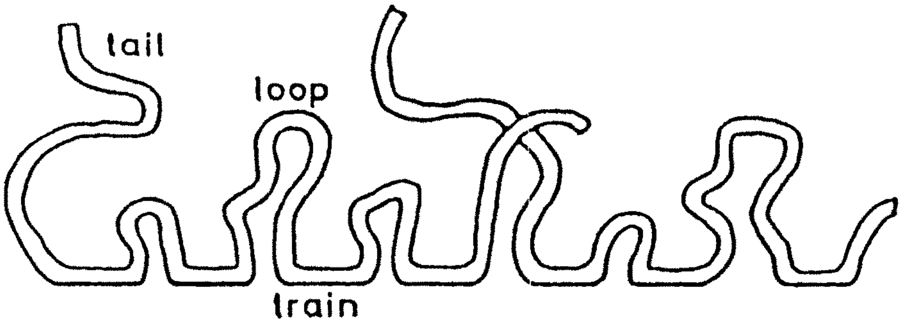


Fig.1.5 Adsorbed polymer molecules with loops, trains, and tails

they may be exchanged]. This has sometimes led to the [mistaken] idea that polymer adsorption is "irreversible".

[3] Polymers are frequently polydisperse in chain length; this leads to fractionation on the surface, "rounded" isotherms and a dependence of the nature of the isotherm on the surface area/solution volume ratio.

[4] Polymer adsorption leads in general to high affinity isotherms. The amount adsorbed rises very strongly at low concentrations and then levels to a pseudo-plateau region.

[5] The adsorption rates are much slower, particularly in the case of polydisperse chains.

Because of the above mentioned differences, it is rather surprising that Langmuir isotherm is still applicable to polymer molecules at low concentration, though not at higher one /73-75/. Freundlich equation has also been used in polymer adsorption, although conflicting reports about its applicability are also seen /76-78/.

Generally, the isotherms obtained for macromolecules have an initial steep slope followed by a plateau region. The interaction between the adsorbent and the adsorbed polymer molecules are reflected on the initial part of the isotherm. The adsorption amount in the plateau region is determined by various parameters like solvent quality /79/, nature of the adsorbent and the chemical composition of the polymers

/80-82/. Fig.1.6 represents a typical adsorption isotherm /79/. Adsorption isotherms with inflection region are also possible and are reported /79,83/. Experimentally, the polymer isotherms are rounded in nature. The adsorbed amount being a function of molecular weight, the plateau region for higher molecular weight polymers extends over the entire experimentally accessible range of concentration /84-90/.

1.5 EFFECT OF MOLECULAR WEIGHT

It is well established, as mentioned before, that the adsorption of macromolecules is an increasing function of molecular weight /91-98/. Adsorption data obtained for narrow molecular weight distributed [MWD] polystyrene samples showed that the adsorbance depended on degree of polymerization, to a power usually less than or equal to 0.5 /99,100/. Thus one would expect better adsorbability for the larger molecules. To our knowledge, Felter and Ray /101-103/ were the first ones to explain the effect of MWD on the amount of polymer adsorbed. As the molecular weight increases, the amount adsorbed tends to a limiting value, and eventually becomes constant /104/. This principle is often used to fractionate polymer samples of moderate molecular weight. A polydisperse sample shows preferential adsorption of large molecules over small ones /105-113/. The driving force for this competitive adsorption is the net entropic advantage gained in returning more number of smaller molecules to the solution than are lost by adsorbing an equivalent surface coverage [but smaller number] of larger molecules /114/. Quantitative predictions have been put forth by Roe /115/ and Fleer et al. /116/. The small

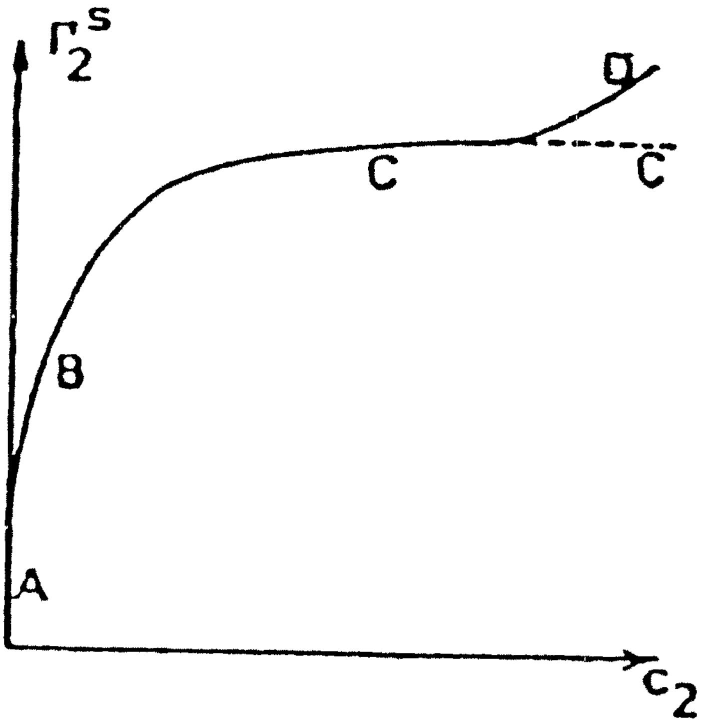


Fig.1.6 Typical polymer adsorption isotherm: A, very low coverage; B, high coverage, lateral interactions; C, plateau, considerable lateral interactions; D, multilayer adsorption [not common]

polymer molecules due to the higher rate of adsorption get adsorbed in the initial stages. As the higher molecular weight polymers are preferentially adsorbed, these smaller molecules get desorbed at a later stage, until an equilibrium is reached /116/. However, if the adsorptional bond is very strong, such a displacement may not occur, resulting in the overall adsorption of smaller molecules. In fact, the preferential adsorption of larger molecules largely governs the thickness of the adsorbed layer /117/.

1.6 EFFECT OF SOLVENT

The overall adsorption process is an outcome of various interactions existing simultaneously in the system. They are [1] polymer-solvent, [2] polymer-adsorbent, [3] adsorbent-solvent, [4] polymer-polymer, and [5] adsorbent-adsorbent interactions. In order to understand the adsorption process fully, individual knowledge of all these interactions is necessary. The solvent nature is a very important factor affecting the polymer adsorption. The conformation of polymer molecules is solvent dependent. It also determines the size and the asymmetry of the macromolecules [i.e. the polymeric coil] in the solution. These factors determine the conditions of contact, the possible orientation, the structure of the adsorbed layer, etc. of the polymers on the adsorbent surface. The size and the shape of the coils depend upon the energy of interaction between the polymer and solvent, and on the inter or intramolecular interactions /117/. The overall enthalpic contribution due to adsorbent-solvent and adsorbent-polymer interactions controls the extent of adsorption. Besides this, the polymer-solvent interaction is also important. Poorer the solvent, higher the adsorption from the solvent. Geometrical factors e.g. the tightening of polymer coils will significantly affect the amount of adsorption. The rise in adsorption in reverse order to solvent power, the latter being a function of intrinsic viscosity and solubility parameter, has also been observed /118/. Desorption of the adsorbed polymer from the same solvent is generally found to be a slow process /119/.

The solvent power can be changed by using different solvents /120-125/. Kawaguchi et al. and several other workers have studied /126-134/ the adsorption from good, poor, and theta solvents. Adsorption of rubbers on silica surfaces, from different solvents is also reported /135,136/. Adsorption of elastomers on carbon blacks from different solvents and sufficiently concentrated solutions has been extensively studied /137,138/.

The solvent power can also be changed by varying the composition of the solvent /139,140/. Though there are many studies of polymer adsorption from single solvent, in practice solvent mixtures are frequently used, as changing the composition of the solvent often induces desorption /141/. Behaviour of sterically stabilized dispersions at times, changes dramatically upon polymer desorption. The mixtures of solvents are used in paint industry to control the effective quality, volatility, and viscosity of the solvent /142/.

In adsorption chromatography binary solvents have also been used for separation of polymers /143,144/. The solvent composition can be adjusted to obtain weak adsorption of a particular polymer vis a vis other polymers, which is a prerequisite for effective separation. Since polymers in a single solvent are usually either not eluted [because they adsorb too strongly] or move with the eluent front [because they do not adsorb at all], solvent mixtures close to the critical point are used, which bring about weak adsorption. This has indeed been supported experimentally by Glockner et al. /145/, Belenky et al. /146/, and several other workers /147,148/. In all mixed solvent systems adsorption/desorption equilibrium exists, the polymer being desorbed by one of the components of the solvent mixture, the so called 'displacer'. The displacement studies are frequently used in determining the segmental adsorption energy. An illustrative example is by Clark et al. /149/ on the conformation of poly [vinylpyrrolidone] on silica from acetone - water mixture. Study of the bulk solution behaviour of polymers, in mixtures of two solvents, has a long history /150-164/. Though entropic effects are generally considered for the adsorption process, enthalpic effects due to the mixture of solvents have also been recently discussed /165/. Studies on mixed solvent systems have been investigated by Marra et al. using the surface force apparatus /166-168/. However, knowledge about adsorption from single solvent is reasonably large compared to that from the mixtures of solvents /169/. The configurational behaviour of chain molecules adsorbed onto a surface is fundamental to the understanding of the macroscopic properties of adsorbed polymer layers. Such behaviour is determined by the chain structure, polymer-solvent and polymer-surface interactions /170/.

1.7 EFFECT OF ADSORBENT

Besides solvent, the surface of the adsorbent has an effective role to play on overall adsorption. Adsorption results only when the interaction between polymer and inorganic oxide exceeds the interactions between polymer and solvent, and between solvent and inorganic oxide. Fowkes et al. /171a/ have proposed a new approach to these interactions, using Drago's /171b/ scale of acidity/basicity. The mode and the extent of adsorption of polymers depend upon the nature of the adsorbent and the adsorbate. This is due to the high specificity of adsorbents in their nature and properties. Adsorbents can be classified according to their surface chemical properties, depending upon their electronic charge distribution on the surfaces. According to Kiselev /172/, adsorbents can be distinguished as : Type I, Type II and Type III. The commonly used adsorbents e.g. silica gel, alumina, and cationic zeolites are of Type II category.

Silica gel consists of globules composed, in a disordered manner, of SiO_4 tetrahedra. This is clearly seen in Fig.1.7[a]. The adsorption properties of silica gel depend on the mutual orientation of the edges of the surface SiO_4 tetrahedra, to which the hydroxyl groups are bound. Owing to the disordered arrangement of surface SiO_4 tetrahedra, the surface 'OH' groups bonded to silicon atoms [$>$Si-OH, silanol groups] are not equivalent as regards to their adsorptivity. Although, the siloxal groups [$>$Si-O-Si$<$] also occur on the silica gel surface, the adsorptive interaction was found to depend on the number and distribution of 'OH' groups per unit area of adsorbent /65,172/.

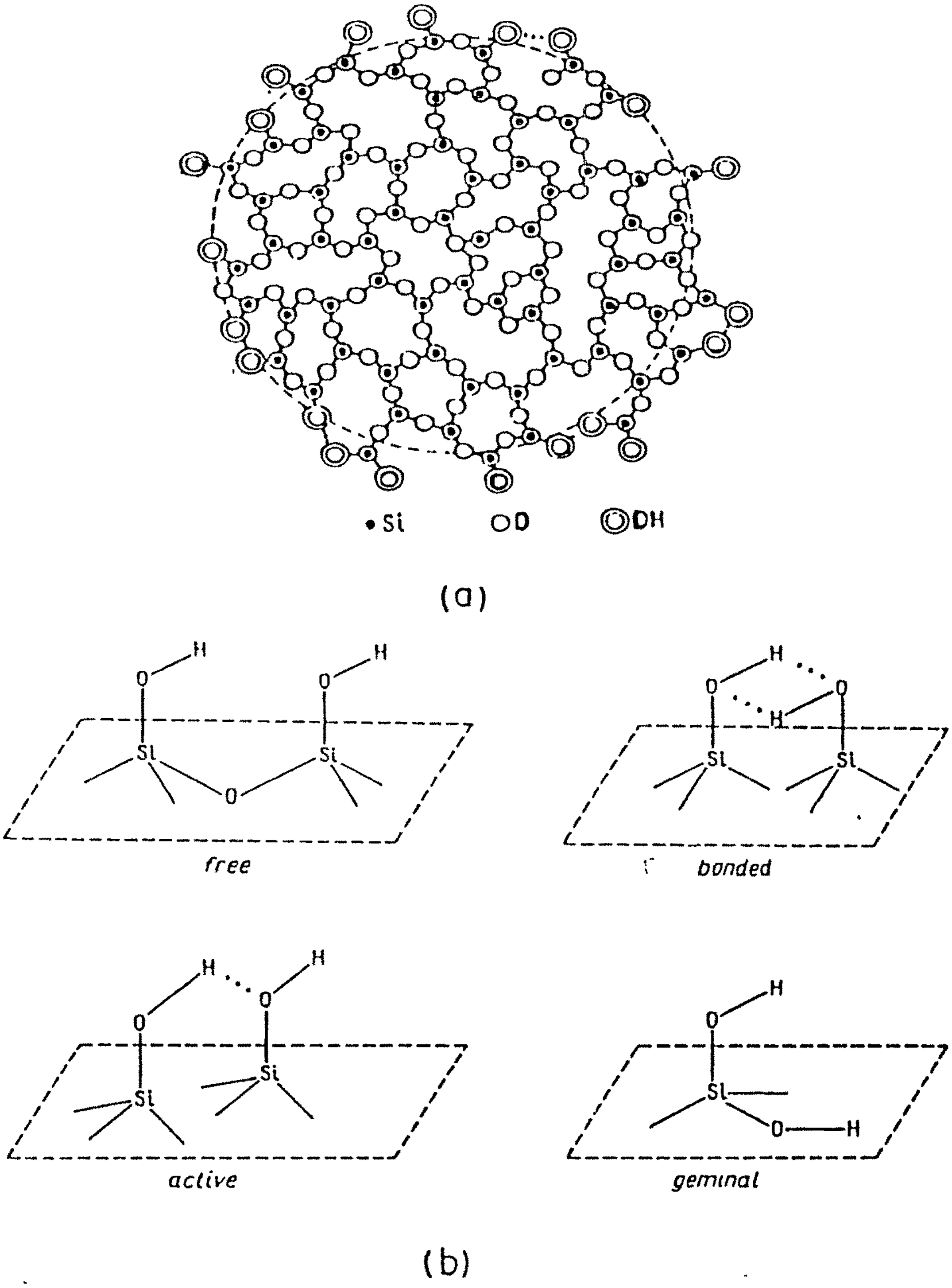


Fig.1.7(a) Globules forming the skeleton of Silica gel /65,171/

(b) Types of hydroxyl groups occurring at the surface of Silica gel

It has been shown by various workers that four different kinds of hydroxyl groups are possible on the surface of the silica gel. These are :

[a] free [isolated] 'OH' Groups
[b] bonded 'OH' Groups
[c] active 'OH' Groups
[d] geminal 'OH' Groups

These are shown schematically in Fig.1.7[b] /144,172-179/. Polyfunctional adsorbate molecules, as well as those possessing delocalized π electrons are more strongly adsorbed on active hydroxyl groups. The monofunctional molecules are adsorbed with equal strength on active and free 'OH' groups /180/. Since the surface hydroxyl groups are responsible for specific adsorption on silica gel /181,182/, surface of these adsorbents should be hydrated to a maximum degree for increased adsorption. The surface concentration of 'OH' groups in hydrated silica gels depends on the temperature of its treatment and not so much on the specific adsorbent surface area. This can be seen from Fig.1.8. As observed from this figure, the concentration of 'OH' groups remains more or less constant between 150-200°C. Between 200-400°C, condensation resulting in evaporation of water occurs, thereby decreasing the number of 'OH' groups and the surface area. Over 400°C, the surface is almost completely dehydrated, hence a very low adsorption capacity /183,184/.

Aluminium oxide, a Type II adsorbent, has recently been thoroughly investigated /185-188/. A model of the Al_2O_3 surface layer structure

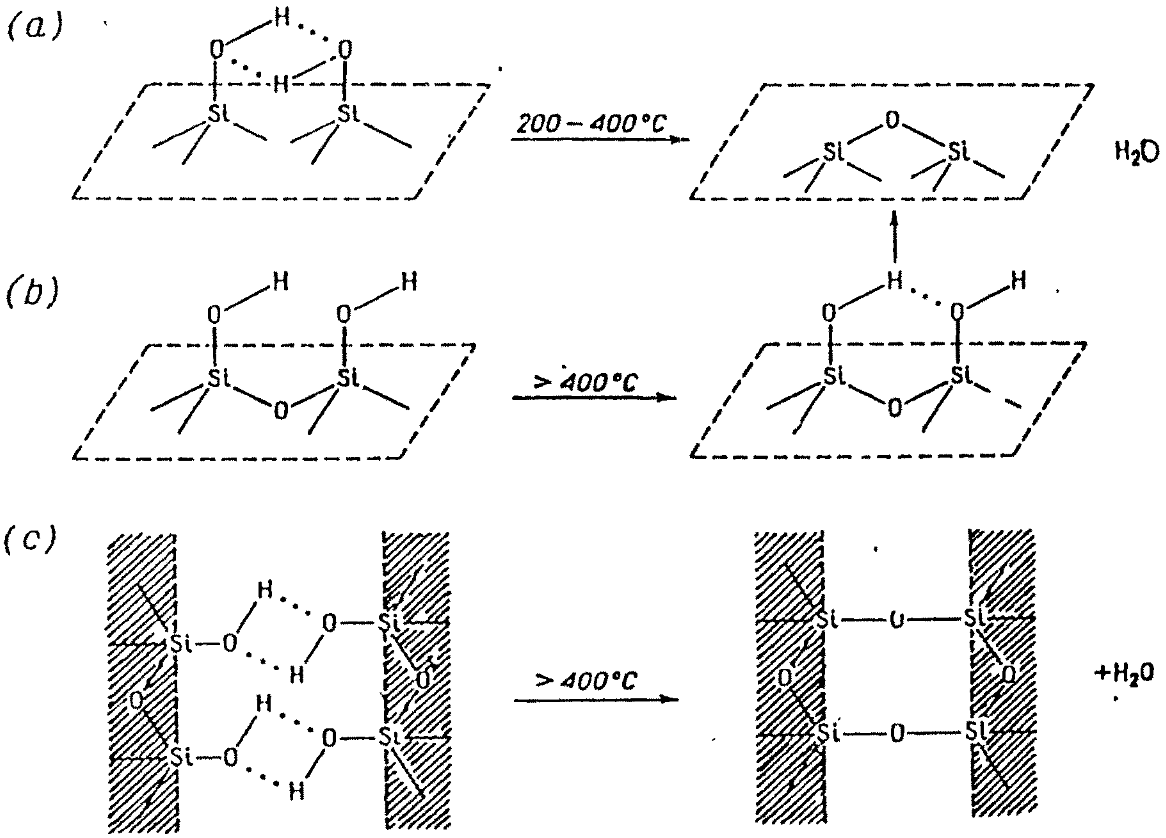


Fig.1.8 Effect of temperature on the hydroxylated silica gel surface

is depicted in Fig.1.9. Flockhardt et al. /189,190/ have postulated the existence of two types of defects on the surface of Al_2O_3 heated to temperatures exceeding 773°K. The first type occurs when there is a deficiency of two or more oxygen ions in the surface layer. At such sites, Al^{3+} ions are exposed in an anomalous way on the surface. Owing to the accumulation of positive charges, such a surface site becomes an electron acceptor [Lewis acid]. The second type is due to occupation of a surface site by two or more oxygen ions. Such defects are of the electron donor type [Lewis base]. This can be seen from Fig.1.10.

Four types of active sites occur on the Al_2O_3 surface /191/ :

[a] Al^{3+} ions [acidic]
[b] O^{2-} ions [basic]
[c] Ionized hydroxyl groups [basic]
[d] Proton defects [electron acceptors]

Most substances are adsorbed on Al^{3+} ions around which a strong electric field exists; molecules liable to polarization [unsaturated and aromatic hydrocarbons] are adsorbed particularly strongly. Their weak localization on Al_2O_3 results in greater selectivity in adsorption of various aromatic hydrocarbons. Moreover, linear molecules are more strongly adsorbed than non-linear molecules.

Adsorption studies of various polymers onto silica surface have been carried out /192-206/. Kawaguchi et al. have studied the adsorption

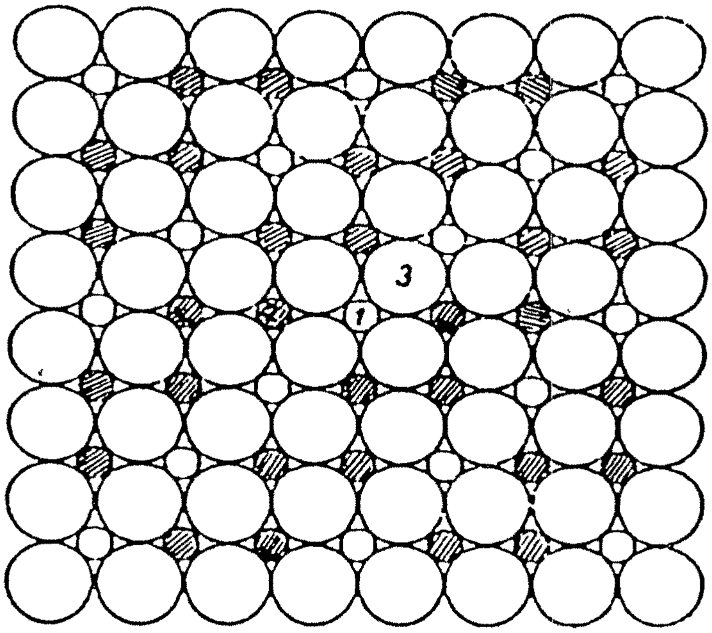


Fig.1.9 Model of -Al_2O_3 surface structure : 1 - surface defects, 2 - Al^{3+} ions, 3 - O^{2-} ions

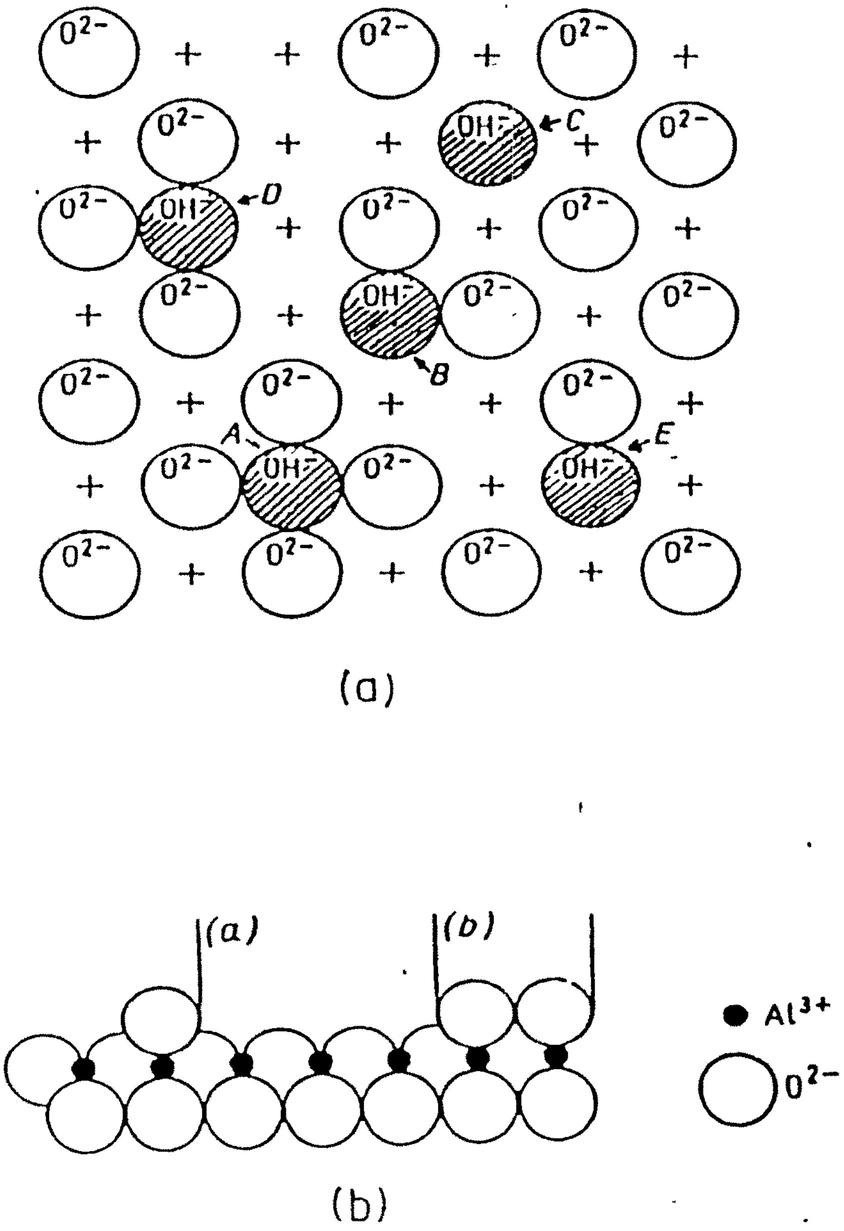


Fig.1.10(a) Model of aluminium oxide after strong dehydration

(b) Surface defects of aluminium oxide heated at 773K : (a) electron acceptor defects, (b) electron donor defects of synthetic rubbers onto different silica surfaces /205,206/. The styrene butadiene copolymer is industrially important, hence its adsorption studies on carbon black or silica particles have been carried out /207-211/. Other adsorbents have also been used for the adsorption study, namely, metal surfaces, mica sheets and zeolites /212/. However, the adsorption of polymers on alumina, to our knowledge, are relatively few.

1.8 EFFECT OF TEMPERATURE

Temperature variations during the process of adsorption increase the mobility and change the flexibility of the macromolecules and the solvent power. The temperature effect is not independent of the solvent and the adsorbent characteristics /123,213-217/. The adsorption either increases or decreases or remains independent with change in temperature. The adsorption of the styrene-butadiene copolymer decreases with temperature /122/. Stromberg /218/ observed the same trend for adsorption of polyesters on glass. The adsorption of poly [methyl methacrylate] from toluene or dioxane solutions on glass, aluminium and silica increases with temperature, adsorption of polystyrene on these adsorbents is practically temperature independent, while the adsorption of poly [vinyl chloride] decreases with temperature increase /70/.

The nature of adsorption of various polymers on carbon are : the adsorption of poly [methyl acrylate] decreases with temperature, that of poly [vinyl chloride] increases, while the adsorption of polystyrene is practically temperature independent /218/ supporting the observation made earlier by Ellerstein et al. /123/. The adsorption of SKN-26 rubber on ferric oxide from toluene solutions, increases considerably with temperature /219/. It has also been observed that /220/, at higher concentration when aggregates are formed, temperature dependence is more marked. The increase in the adsorption of the SKN-18 and SKN-26 rubbers might be due to thermal deaggregation of the molecules, so that the rubber macromolecules can penetrate more readily in the pores of the adsorbent.

Hence it is clear that every system behaves in an independent manner and it is difficult to generalise the overall adsorption behaviour with respect to temperature change. Therefore we decided to study the effect of temperature variation on the extent of adsorption.

1.9 THERMODYNAMICS OF ADSORPTION

Thermodynamics is applicable to all forms of the energy changes associated with physicochemical processes. It helps in predicting the extent and the direction in which a chemical reaction, or for that matter, any process would proceed /221/. The state of the thermodynamic equilibrium in adsorption process on solid/liquid interface is characterized by interfacial mass transfer, which involves adsorbed species and those in solution /222/. A very important problem in the study of adsorption of polymers is to obtain thermodynamic parameters of the adsorption process from the experimental data obtained for various systems. This problem is much more complicated for high molecular weight systems than for low molecular weight ones /223-225/.

The existence of multiple contact points between polymer and adsorbent /226,227/, leads to reasonably high adsorption enthalpies. Secondly, the polymer-polymer entanglements in the diffuse zone constitute a kinetic limit to the polymer desorption. The application of equilibrium thermodynamics to polymer adsorption is therefore difficult. Some authors are of the opinion that typical equilibrium condition is not achievable in case of polymer adsorption, hence the equilibrium thermodynamics can not be used /224/. Scheutjens et al. have however proved beyond doubt the efficacy and justifiability of such use /105/.

The free energy of adsorption is calculated from the equilibrium constant. In the three component system, i.e. polymer, solvent and adsorbent, various interactions exist, resulting in a complicated system. The determination of enthalpy change associated with each of these interactions is therefore very difficult. Some of these can of-course be determined by microcalorimetry /227/. Therefore, the enthalpy of adsorption determined from the free energy of adsorption is the overall enthalpy of adsorption, a resultant of all the individual enthalpic contributions in the system. The free energy of adsorption $\triangle G_{ads}$ can be calculated at various temperatures from the equilibrium constant data. Using well known thermodynamic relation, the entropy $\triangle S_{ads}$ and the enthalpy of adsorption $\triangle H_{ads}$ can hence be computed. To compare the data for various systems, a single reference state is preferable. The reference state chosen for this study was a hypothetical infinitely dilute solution, where the concentration of polymer [in the scale used] was unity. The thermodynamic quantities at infinite dilution can thus be evaluated and compared. These quantities were termed as ΔG^{o}_{ads}, ΔH^{o}_{ads} and ΔS^{o}_{ads}. As these quantities are inherent characteristic of a system, they form a sound basis for comparative study.

1.10 KINETICS OF ADSORPTION

A study of the kinetics of adsorption is of fundamental importance for understanding its mechanism. The rate of establishment of equilibrium during adsorption depends on the chemical nature and molecular weight of the polymer, the solvent, and the type of adsorbent. In most cases, the kinetic curves indicate an increase in the amount of adsorbed polymer with time, with the equilibrium value being approached asymptotically. Some unconventional type of .kinetic adsorption curves have also been reported /228/.

The diffusion of polymers to the surface of the adsorbent or into its pores is almost always the stage that determines the adsorption rate. Stirring during adsorption usually increases the rate at which the system approaches equilibrium. This is shown for PMMA and PS on silica gel from trichloroethylene /229/. Porosity of adsorbent affects the rate of attainment of equilibrium /230/. Hobden et al. /74/ have shown that longer time is required for establishment of equilibrium in polystyrene-charcoal systems. During adsorption of copolymer of styrene with butadiene, butyl rubber, and natural rubber on carbon blacks of various types, equilibrium was established within 18-90 hours. The time depended on the nature of the polymer, the specific surface of the carbon black and other variables. The highest adsorption rate was noted for butyl rubber and the lowest for natural rubber. The adsorption rate decreased with increase in specific surface /41/. This is because the porosity hinders the rapid penetration of the macromolecules to the inner surface of the carbon black. Koral et al. /124/ have shown lesser adsorption rate of poly [vinylacetate] on irregularly shaped alumina than its adsorption rate on the smooth nonporous surfaces of iron and tin.

Kiselev et al. /231/ noted a decrease in the adsorption rate with decrease in concentration of the solution. Adsorption rate on smooth surfaces thus increases with decrease in concentration and on stirring /232/. Adsorption rate is also affected by molecular weight, molecular weight distribution, temperature, amount of solution, and several other parameters. In most of the cases, the adsorption rate decreases with increase in molecular weight /233/. The adsorption rate of poly [dimethyl siloxane] on silica also depends very strongly on the molecular weight /234/. In case of polybutadienes with narrow molecular weight distribution, the adsorption rate on carbon black from heptane solutions /235/, decreases with increase in molecular weight. However, opposite effect is observed for polybutadienes of higher molecular weight. This is probably due to inaccessibility of the adsorption surface to large molecules. Thus no unambiguous conclusion can be drawn from the data available on the effect of the molecular weight and the concentration on the rate of adsorption from solutions. Recent studies on kinetics have shown conformational changes in the molecules of the adsorbed layer. The time required to attain equilibrium, i.e. to attain a metastable conformation, of course varies from system to system /236,237/.

1.11 EXPERIMENTAL DATA AND VARIOUS PROPOSED THEORIES

The domain of polymer adsorption on solids can be characterized as a state of confusing developments. The developments include increasingly sophisticated theories and experiments. There has been a plethora of theories of polymer adsorption in recent years, atleast for linear chains adsorbed on regular surfaces. Computer simulations and analytical methods have been used, based on diffusion equation, partition function, and scaling theory approaches. The first theories on polymer adsorption treat the case of an isolated chain on an adsorbing surface, both on a lattice and in continuous space /238-250/. All these theories had one thing in common, that is, the formulation of partition function for the polymer molecule at an interface, and hence the calculation of structure of that molecule corresponding to its minimum free energy. In these models, the segment-surface interaction and the conformational statistics of an adsorbed molecule, consisting of trains, loops, and [sometimes] tails, is considered in detail, but the segment-segment and intermolecular interactions are neglected. Since the chains do not "feel" each other, there is no limit to the number of segments that can be accomodated on the surface, hence the adsorbed amount increases linearly with increasing solution concentration /245/. Even in very dilute solutions, the segment concentration near the surface is usually so high that the direct surface coverage approaches saturation. Such arguments helped in the calculation of the isotherms, etc. The main drawback being that the model of a polymer at an interface had to be constructed in order to facilitate the calculations and the extreme simplification in the models to fit into the results. Thus, the diversity in the assumptions led to vastly different results. Though these theories provide a suitable starting point for more realistic models, they have little relevance in practice. Therefore, it is imperative to include the segment-segment and segment-solvent interactions. The various theories proposed to account for the above interactions are by [a] Hoeve /251-253/, [b] Silberberg /254/, [c] Roe /255/, and [d] Scheutjens and Fleer /256-258/. The theories of Hoeve and Silberberg start from the statistics of an isolated chain, wherein the end effects [tails] are neglected. These theories account for polymer-solvent interaction using the ideas of the Flory-Huggins theory for polymer solutions /259-261/.

Roe, Scheutjens and Fleer /255-258/ derive the partition function for a mixture of free and adsorbed polymer chains, and solvent molecules by calculating the number of ways in which the chain and solvent molecules may be arranged in an arbitrary but [fixed] preassigned concentration gradient near the surface. The equilibrium concentration profile is obtained on maximization of the partition function. Moreover, Flory-Huggins model is used to account for the segment-segment and segment-solvent interaction. The Scheutjens and Fleer theory calculates the complete distribution of polymer conformations near the surface [including those in which tails are present], whereas Roe's model gives only the overall segment concentration profile, without information about the distribution of trains, loops and tails. The Scheutjens and Fleer model stands apart in describing many aspects of polymer adsorption, theoretically, in considerable detail /262-266/. All the above mentioned theories predict polymer adsorption isotherms with an initial steep rise followed by a nearly horizontal semiplateau. An analysis of all the theories of polymer adsorption shows that the application of contemperory ideas on the structure and properties of polymers and methods of statistical mechanics have appreciably helped in predicting the adsorptional behaviour of polymer. However, no universal equation of the adsorption isotherm can be derived. This indicates the complex and many sided phenomena accompanying adsorption /267,268/.

No doubt, the computer simulations provide both, a qualitative and quantitative means of understanding the factors that influence polymer-surface interactions /269,270/. By viewing the graphical output, one can unravel the complex series of events that occur at an interface. The quantitative features characterizing the interfacial region, e.g. fraction of polymer molecules bound to the surface, thickness of the adsorbed layer, the conformation and dimension of the bound and free chains, etc. can be evaluated and computed at any point of the process. Consequently, the information on the kinetics of adsorption as well as the knowledge about final equilibrium state can be obtained. Recent publications /271-275/ have described the computer simulation in detail for the homopolymers and copolymers, making the theoretical appraoch to polymer adsorption quite feasible.