CHAPTER-I

INTRODUCTION

1.1 GENERAL INTRODUCTION

Ever since the discovery of plastics more than a century ago, the pace of polymer science and technology has been accelerating dramatically. Astonishing progress has been made, particularly during the last few decades, in elucidating the nature of macromolecules, the mechanism of their formation and in devicing entirely new class of giant molecules. Man's ingenious approach has deviced various practical methods of synthesizing these macromolecules and innumerable ways of employing these for human benefit.

The development of filled and reinforced plastics and its technological importance led to studies of adsorption of polymers on various substrates almost three decades ago. The adsorption of polymers from solutions can be considered as one of the most important fields in the physical chemistry of polymers /1/. Most of the modern polymeric materials are heterogeneous systems with highly developed interfacial areas. These include reinforced plastics, filled thermoplastics, reinforced rubber, varnish-lacquer coatings, glued joints etc. Here, the polymers come in contact with solid bodies changing the surface properties due to adsorptional interaction. Hence the adsorption of polymers at solid-liquid interface became the subject of detailed experimental and theoretical studies. This accounts for the plethora of publications in this field by many scientists /2-20/.

Adsorption is a phenomenon associated with the preferential accumulation of materials at an interface /21/. The interaction between the surface and the adsorbed species may be either chemical or physical. Various types of interactions/bondings have been identified in the adsorption process /22, 23/. The net adsorbent-adsorbate interaction involves more than one type of force depending on the chemical structure of the components.

Polymer adsorption and the adsorption of small molecules differ drastically in many respects /24/. The macromolecules can assume large number of configurations in the bulk solution as well as at the interface owing to the large size of the macromolecular chains. The configuration was suggested to be in the form of trains, loops and tails /25/ as illustrated in fig. 1.1

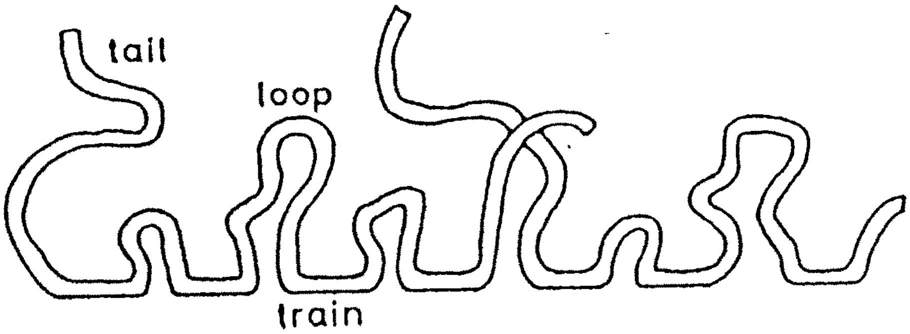

Fig. 1.1 Adsorbed Polymer Molecules with loops, trains and tails/24/.

A train is a series of consecutive segments, all in contact with the adsorbent surface, loop consists of segments only in contact with the solvent and is bound to a train on each side. Tail is terminally bound to a train with the other end dangling in solution. Thus loops and tails have a three dimensional look and are not in direct contact with the surface. Unlike in monomolecular adsorption, the entropy loss per molecule of polymer is high /26/, the change in enthalpy is also very high due to the many possible attachments per chain. So apart from the determination of the adsorbed amount, information is required on the bound fraction, layer thickness and segment density distribution of the macromolecular adsorption /27/.

The free energy change associated with the transfer of a particle to the surface from a solution is same irrespective of the particle size. The particle is retained if such an interaction produces sufficient decrease in free energy, over coming the single particle effect /27/. Hence macromolecules which have large surface area and high surface activity are preferentially retained. Even when the individual group contribution is less, strong positive adsorption is inherent. Due to the large number of molecules on the chain their attachment to the surface is favoured and therefore the surface can become necessarily saturated even at low concentrations /28/. This is one of the most distinguishing features of macromolecular adsorption.

When the macromolecules get adsorbed onto the surface, large number of solvent molecules get displaced leading to an entropy gain; when the macromolecules adsorb onto the surface there will be entropy loss. These two phenomenon together will control the overall entropy value. Equilibrium is reached much slower because of the slower rate of surface reaction, diffusion of the polymer through the solution and the preferential adsorption of the larger chains /28,29/. The time to reach equilibrium vary from few minutes to many hours depending on the polymer species and on the characteristics of the adsorbent.

The equilibrium is reached quickly at the interface in a gas-liquid and liquid-liquid systems due to mobility. But the boundary region between a solid-liquid interface is distinct, because the surface structure and shape for this system is controlled by the arrangement of the molecules in the crystal lattice at the interfacial region of the solid. The shape of the surface is not smooth like the liquid-gas interface. In most cases the solid-liquid interface is highly heterogeneous in structure in multiple directions /30/, and possesses a tendency to assume minimum surface area after the rearrangement of the crystal forces. Hence solid-liquid interface requires longer equilibration time than gas-liquid and liquid-liquid intefaces, making the thermodynamic treatment of the adsorption process more complicating /31/. Thus when the flexible polymer is placed near or onto a surface, great distortions of its shape is expected depending on the chemistry and reactivity of the groups and on the heterogenity of the adsorbent surface /32/.

There are five major factors deciding the extent of polymer adsorption from solutions /33/.

(i) polymer - solvent (ii) polymer - adsorbent

(iii) adsorbent - solvent (iv) polymer - polymer

(v) solvent - solvent

The balance of these five interactions finally determines the extent of adsorption and the nature of the adsorption isotherm.

1.2 APPLICATIONS

From alchemical days of chemistry to the present days large scale chemical industries, adsorption phenomena has helped in the progress of technological and industial developments. Most of the heterogeneously catalysed reactions /34, 35/ like synthesis of ammonia, manufacture of synthetic petrol etc. are effected through adsorption of reactants on solid surfaces. Chromatographic methods, which are widely used now-a-days in separating and analysing valuable and minute quantities of components from a mixture are also based on adsorption /36/. The successful separation of rare earth elements by chromatographic method using fractional adsorption on organic resins /37/ is an outstanding example.

With the development of polymer science during the last few decades, adsorption studies of the macromolecules on surfaces particularly at the solid-liquid interface have gained importance owing to its technological and academic interest /38, 39/. The major fields of application include soil phenomena, tertiary oil recovery /40/, biomembranes /41/, adhesion, corrosion control, detergency, lubrication, drag reduction, film deposition etc.

Reinforcing and/or cost reducing fillers are exclusively used in rubber products like tyres, tubes, gaskets etc. and also in many high performance plastics like reinforced plastics, thermosets, composites and many others. The final mechanical and physical properties of these are governed by the adsorption phenomena occuring at the interface between the filler and the polymer. The intraction of polymeric materials with solid bodies appreciably changes all the properties of polymer because polymer-solid body interface is mainly adsorptional in nature /42/. The properties of composites and high performance engineering plastics are governed by the polymer-filler interactions /43/.

The use of adsorbed macromolecules in stabilizing the colloidal dispersions has a long history and much technological importance /38, 39, 44,45/. Considerable attention has been paid to the polymeric stabilization of dispersants in paints, inks, pharmaceuticals and in food stuffs /38, 46/ where the polymer adsorption characteristics control the stability of colloidal suspensions.

Polymer adsorption is equally important in aggregation and flocculation processes /47/. Polymeric flocculants are now an essential part of sludge processing operations such as thickening and dewatering. The design of polymeric flocculants for particular systems and its optimum use requires a theoretical understanding of adsorptional interaction between the adsorbed polymer layers and the effect of these interactions on dispersion stability /48/.

Certain materials of technological importance like finished textile fibers, coated polymer films and impact resistant polymer blends contain interfaces between dissimilar polymers /49/. Adsorptional interactions control the ultimate physico-mechanical properties of these materials.

The interfacial properties of dilute polymer solutions are of fundamental importance in diverse fields such as foaming, coating, printing flows, porous media flows and hydrodynamic lubrication /38/. The formation of glued joints, the application of varnish-lacquer coatings include adsorption of polymers on the surface as the first stage.

Surface phenomena are important in solving problems in application of polymers to medicine /50/, biochemistry, bioengineering, immunochemistry and other fields. Here the adsorptional phenomena occurs with the interface of living tissues, as in modification of biocompatibility of artificial implants, cell adhesion etc.

Hence polymer adsorption studies are of immense importance due to many applications in medical and technological fields.

1.3 ADSORPTION ISOTHERMS

The shape of the adsorption isotherm provides qualitative information on the nature of the solute-surface interaction. The strength of the solute-surface bond varies over a wide range from the weakest van der Waals forces' to the strongest chemical adsorption, and all types have been observed in studies of adsorption from solution /22/. The time taken to reach equilibrium is normally indicative of the type of interaction except in case of porous adsorbents where the pore filling would be slow. At room temperature chemisorption is usually a much slower process than physical adsorption. Physical adsorption is very common and the specific nature of the interaction is usually implied from the chemical nature of the materials involved. Energies of interaction provide important supplementary information. Their interpretation may be difficult because they refer to the exchange process involving both solution components, where the entropy factors are dominant /22/.

Adsorption isotherms of solids from solutions have been classified by Giles et al. /51, 52/ and have related the adsorption mechanism, orientation of the adsorbed molecules and orientation change etc. to the shape of the isotherm. The classification is as shown in Fig. 1.2. In this the class H isotherms correspond to adsorption of very

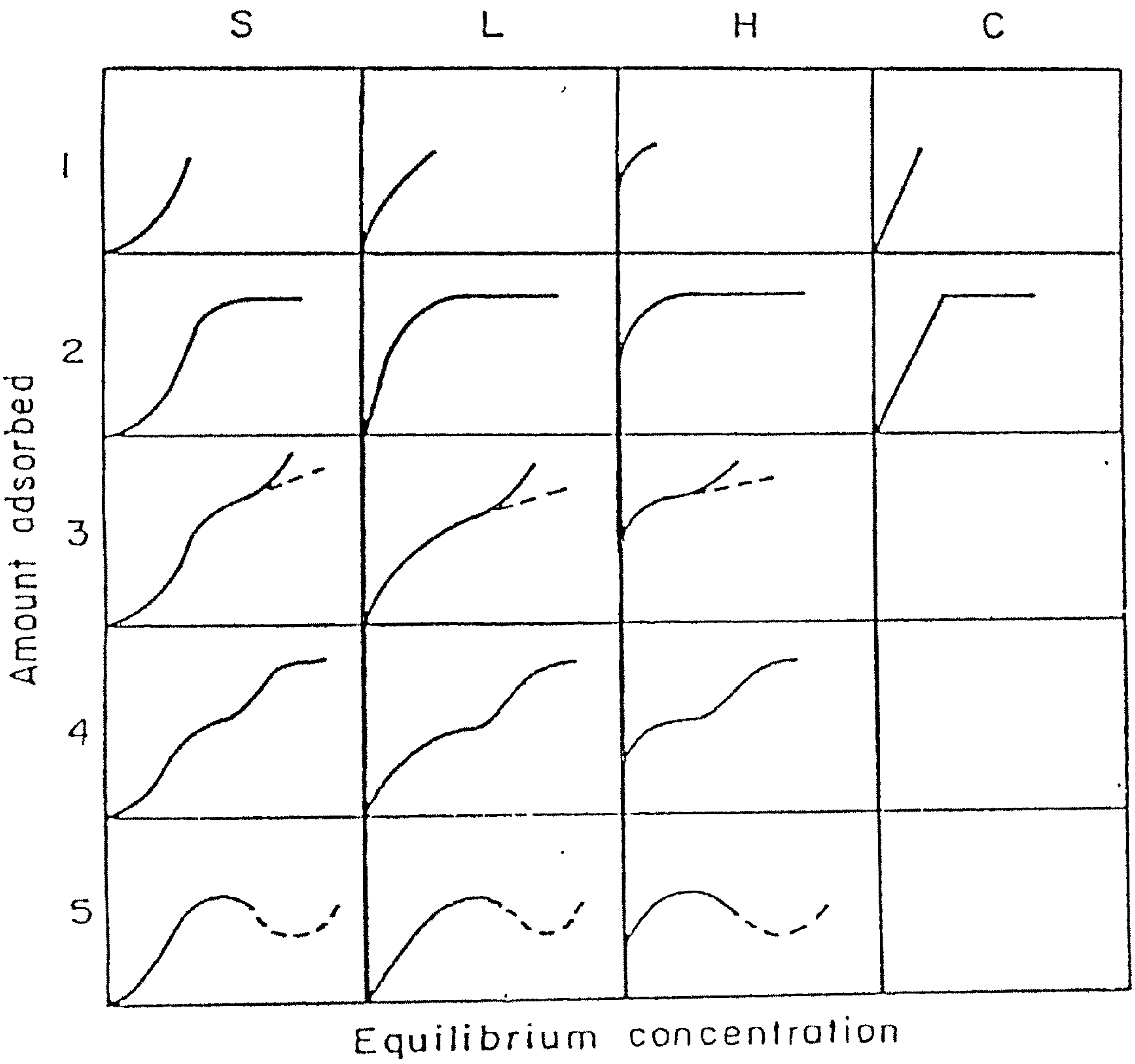

Fig. 1.2 : Classification of isotherm shapes/51.52/

large molecules like the polymers. The subgroups relate to the shape of the isotherms /53/ at higher concentration.

Generally, the isotherms obtained for macromolecules have an initial steep slope followed by a plateau region. The initial part of the isotherm reflects the nature of the interaction between the adsorbent and the adsorbed polymer. Fig. 1.3 represents a typical adsorption isotherm /13, 54/.

The adsorption amount in the plateau region is determined by various parameters /54-63/ like the solvent quality, nature of the adsorbent and the chemical composition of the solute.

Adsorption isotherms with inflection region are also possible /64/ as shown in Fig. 1.4 and are caused by the change of orientation of the adsorbate molecule on the adsorbent surface with variation of equilibrium concentration.

Our investigation, presented in this thesis, also revealed that the adosrbent characteristics has a predominant role in determining the shape of the isotherm.

Though there are many differences between the properties of low molecular weight substances and high molecular weight substances, it would be rather surprising to find that the adsorption isotherms derived for low molecular weight systems are applicable to high

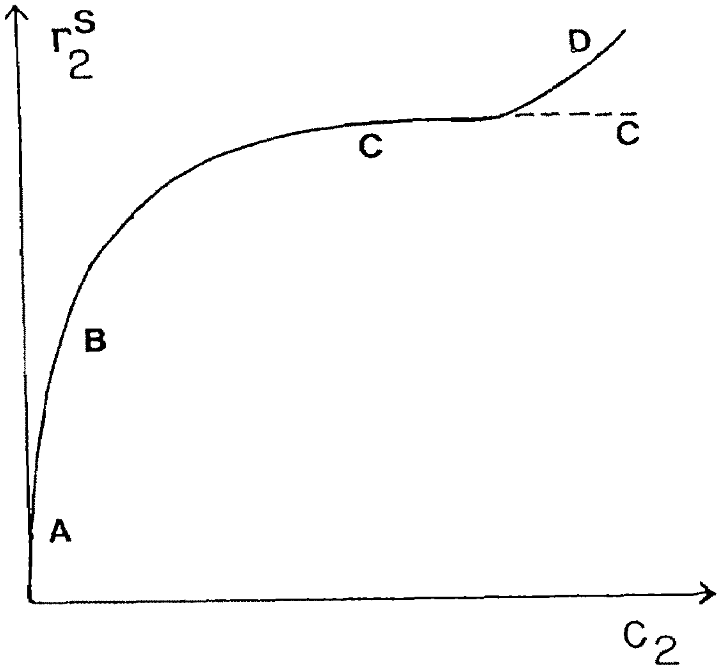

Fig. 1.3 : Typical polymer adsorption isotherm A, very low coverage B, high coverage, C, plateau, considerable lateral interactions, D, multilayer adsorption.

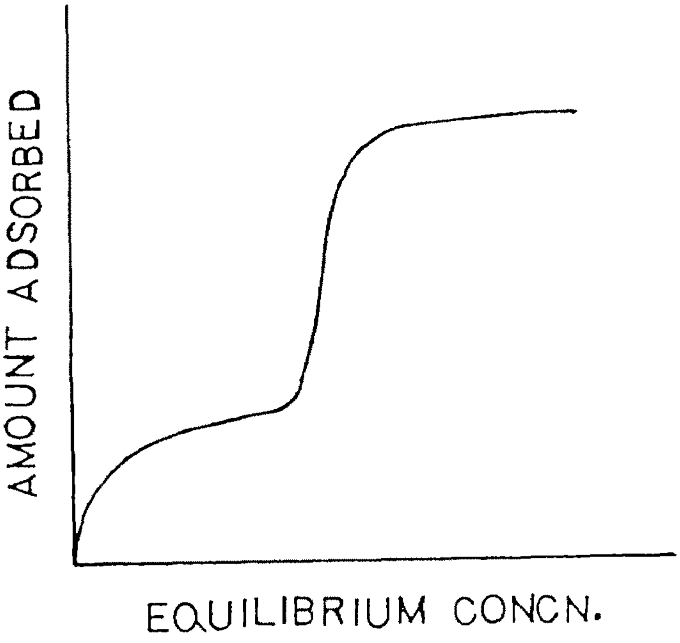

Fig. 1.4 : Adsorption isotherm with inflection region.

molecular weight ones also. Many attempts have been made to apply the Langmuir equation for isotherms to polymeric systems. At low concentrations they agree fairly well but at higher concentrations the agreement is poor /65-67/. Attempts have also been made to apply the Freundlich equation to explain adsorption isotherms. Although Gyani /68/ found satisfactory agreement between the experimental data and the Freundlich's equation for polysaccharides on activated charcoal, in general the agreement is poor /69, 70/, especially at low concentrations.

Another factor deciding the isotherm shape is the polydispersity /29, 71-73/. The isotherms of polydisperse samples leave the ordinate axis at low adsorptions and is more rounded. Recently Cohen Stuart et al /29/ have explained the effect of polydispersity and adsorbent concentration on the shape of the adsorption isotherm.

Many publications have revealed the average molecular weight dependence on the plateau region /74-80/. Generally the amount adsorbed increases with the increasing molecular weight of the polymer. Moreover, solvent quality and amount of adsorbent are also important /81/. Degree of rounding is less pronounced from good solvents because then the adsorbed amount depends weakly on molecular weight /29, 82/. The shape of the adsorption isotherm is independent of the surface area of the adsorbent, because isotherms give the relationship between two intensive quantities namely the surface concentration and the solution concentration. But there are examples which demonstrate that sharper isotherms are found when less adsorbent is used /29, 83/. Other phenomena like multilayer adsorption /84/, spreading etc. induce deviations from the general trends of the adsorption isotherms.

Experimentally obtained isotherms usually show a gradual increase of the adsorbed amount with concentration usually denoted as a rounded isotherm /29/, unlike the sharp isotherms predicted by theory. The amount of polymer adsorbed per unit surface increases rapidly with equilibrium polymer concentration in the solution and reaches a plateau value.

1.4 SOLVENT CHARACTERISTICS

The solvent plays a major role in deciding the polymer adsorption at the solid-liquid interface because the conformation of the polymeric chains in the solution depends on the quality of the solvent. Many important factors like the condition of contact of the polymeric molecule with the adsorbent, the orientation of the macromolecular chains on the adsorbent surface, the structure of the adsorbed layer etc. are determined by the size and shape of the macromolecules in solution. The size and shape of the polymeric coils are dependent on the energy of interaction between polymer and the solvent molecules and on intramolecular interactions. The polymer-solvent interaction parameter (χ) is defined by Flory-Huggins theory /85/. This theory also correlates the interaction parameter (χ) and chain size and is based on the concept of Osmotic action of the solvent on the polymeric molecule present in the shape of a statistical coil. χ determines the solvent power.

There are various methods to evaluate the solvent quality like intrinsic viscosity $|\eta|$, solubility parameter (δ) and eluotropic series. Shultz /86, 87/ showed that the intrinsic viscosity is related to the solvent power. Koral et al· /88/ found that for a large number of systems adsorption increases as $|\eta|$ decreases. In adsorption of poly (vinylacetate) on iron from various solvents they observed that no adsorption occured from chloroform, a good solvent which had the highest intrinsic viscosity. We also observed /89/ a similar increase in adsorbed amount in polybutadiene-cyclohexane system on alumina and silica gel where the $|\eta|$ was less than that of toluene. But Luce and Robertson /90/ could not establish any distrinct correlation between the maximum value of adsorption and intrinsic viscosity. They could establish certain correlation between the solubility parameter and adsorption, but a clear relation was not forthcoming.

Another criterion for determining the solvent power is the solubility parameter (δ). When the difference in δ i.e. $\Delta\delta$ for polymer and solvent is high, the solvent is poor. Mizukara et al· /91/ observed a linear relationship between the adsorption values and the solubility parameter.

surface /94/. This has been observed in case of adsorption of poly (dimethyl siloxane) on glass from acetonitrile-benzene mixture where acetonitrile had strong affinity for glass.

Effect of the solvent power has been studied experimentally for many adsorption systems. Kawaguchi et al. /95, 96/ have carried out various studies on adsorption of polystyrene in good, bad and theta solvents. Several others /97-102/ have also done similar studies.

Though the study of polymer adsorption from single solvent has received much attention, in practical applications solvent mixtures are frequently used. Binary solvents are particularly interesting, because upon changing the composition of the solvent, desorption of polymer may occur/103/. Such studies have wide application in paint industries where mixture of several solvents are employed in order to control the effective solvent quality, the volatility and viscosity/104/. Marra et al. /105,106/ have investigated the effect of mixed solvents using the surface force apparatus. However, knowledge about adsorption from mixed solvents are less compared to that from single solvents /106a/.

Fowkes et al/107/ have formulated a different approach to explain the adsorption phenomena. They have explained the solvent-polymer, polymer-adsorbent and the adsorbent-solvent interactions on the basis of acid-base interactions. Studies by Gregg et al/108/ showed that dimethyl formamide [DMF] being polar and basic the affinity is more for aerosil silica and found that addition of DMF to the solution of polymer markedly reduces adsorption due to the adsorption of DMF on acidic adsorbent.

1.5 ADSORBENT CHARACTERISTICS

The chemistry of the surfce cannot be ignored when embarking on measurements of adsorption from solution/22/. The chemical character of the adsorbent surface determines the nature and energy of interaction between the adsorbate molecule and the adsorbent. There are many factors which decide the orientation of the molecules on the surface at the time of adsorption. Detailed knowledge of inter-molecular interactions between the adsorbent surface and the solute molecules in solution are required to predict the precise quantative rules to explain the orientation of the molecules at the surface.

Kiselev et al. /109,110/ systematically studied the effect of the chemical nature of the adsorbent surface on the adsorption of polymers from solution and also modified the surface which enabled them to determine the effect of chemical nature of the adsorbent surface on adsorption characteristics. Such alterations can drastically effect the adsorption process. For example by reducing the number of surface hydroxyls the solvent-adsorbent interactions could be reduced to a large extent to favour more adsorption of the polymers. Specific surface area of the adsorbent is also an important factor.

Kraus and Dugone/111/ showed that copolymer of styrene-butadiene adsorb more with increasing specific surface area of the adsorbent. Adsorbents with similar specific area but different chemical nature have different adsorption capacity. The presence of surface impurities like water molecules etc./94/ on the surface can hamper adsorption process. It is the usual procedure to activate the adsorbents at 150-200°C. This treatment desorbs the water molecules without much affecting the properties of the adsorbents. It was also observed that activation at elevated temperatures reduced the number of hydroxyl groups on the Silica surface and reduced the adsorption of polar molecules sharply/112/.

Inspite of the availability of the vast literature /67,74,113-116/ dealing with adsorbent characteristics vis-a-vis polymer adsorption, it is difficult to compare the results obtained by various investigators working with adsorbents of the same type. This is because the method of preparation and the specific surface characteristics differ largely affecting the adsorption phenomena.

Kiselev/117/ has characterized the adsorbents according to their surface chemical character taking into account their electronic charge distribution on the surface.

According to this classfication there are three types of adsorbents :

They are,

Type I - non specific adsorbents where there are no functional groups or exchangeable ions eg. graphitized carbon black, saturated hydrocarbons, polyethylene etc.

Type II - Specific positive adsorbents. They have OH groups of acidic character at their surface eg. SiO_2 nH_2O.

Type III - Specific negative adsorbents. These have on their surface, bonds or groups of atoms with a negative charge concentrated on their peripheries, eg. a substance with a suitable functional group like CN^-.

The adsorbents studied in the present thesis are alumina, silica gel and calcium carbonate. These can be classified as Type II adsorbents. The characteristics of these are to be discussed in Chapter III. As the adsorbent characteristics are more stressed in the present investigation, these three adsorbents which had dissimilar surface characterstics, e.g. surface area, chemical composition and surface geometry etc., were chosen.

1.6 ADSORBATE CHARACTERISTICS

Several features of solute structure are relevant eg. chain length, ring structure, nature of polar groups and physical state in solution /22/. In case of adsorption of small molecules, many publications have discussed the effect of chain length, for example fatty acid adsorption on charcoal/118/, dicarboxylic acids [C_2-C_{10}] on spheron 6 /119/ and methyl esters of n-fatty acids on silica/120/. The trends obtained were not always comparable. Crisp/121/ studied the adsorption of long chain alcohols [C_{16}, C_{18} and C_{31}] on alumina from benzene solution and found no chain length effect, and the heats and free energies of adsorption were found to be independent of chain length. The effect of increasing the number of aromatic rings in the molecule was demonstrated by Kiselev and Shikalova /122/. The fraction of hydroxylated silica surface covered at a given concentration of benzene, naphthalene and phenanthrene in n-heptane solution increased with the number of aromatic rings.

As in simple molecules, so also, in polymers the chemical nature of the macromolecules, their shape and size in solution have a dominant role to play in understanding the adsorption process. In a given mixture of equivalent macromolecules the larger molecules get adsorbed better/29/. This phenomenon is particularly more observed in the higher concentration region, where as in the lower concentration region, the lower molecular weight fractions also get adsorbed. The rate of adsorption of shorter chains are greater than that of longer ones due to diffusion. So at the initial stage they are adsorbed and then displaced by larger ones depending on the thermodynamic equilibrium state. This may not happen when the adsorption bonds are stronger as in chemisorption. For a complete analysis of the results, information on the actual size of the molecules penetrating into the pores are necessary, even then it is difficult and lacks reliable dependence of the adsorption on the molecular weight.

The effect of molecular weight on the adsorption process has been the subject of many investigations. The results are inconclusive. Although some observations/123-131/ reveal an increase in adsorbed amount with higher molecular weight, contrary observations have also been reported /132,133/. Constant adsorption with increasing molecular weight was reported by Bonekamp et al/134/. This variation seems to be a function of the adsorbent surface characteristics.

When molecules adsorbing to the surface undergoes a conformational change, groups are exposed and sites are created to which a second layer of macromolecules can adsorb. In fact, the process could be repeated forming multilayers. The potential for multilayer formation is more observed in case of compact copolymers/27/, which are prone to undergo conformational change upon adsorption. Steric hindrance in the polymer molecules will tend to reduce the strength of bond between polymer and the substrate.

Copolymer adsorption studies /135-146/ have gained momentum in the last decade owing to their superiority in some properties to the corresponding homopolymers. A literature survey revealed that adsorption studies of random copolymers as a function of chemical composition of the copolymers are few and far between/136,138/. In the present thesis, thermodynamics of adsorption of random copolymers will be discussed.

1.7 TEMPERATURE EFFECT

The temperature dependence of adsorption is complex and depends on the solvent and adsorbent characteristics/147-151/. A temperature increase may lead to either an increase or decrease in the solvent power and this parameter does not always effect the adsorption in the same way. Temperature rise during adsorption increases the mobility of the macromolecules, changes the solvent power and also affect the adsorption of the solvent competing with the adsorption of the polymer.

The adsorption either increases or decreases or remain independent with the change in temperature. Stromberg/152/ found that the adsorption decreases with. increase in temperature for poly (neopentyl silicate) on glass from toluene. This he explained on the basis of increasing solvent power with the increase in temperature. But for the same polymer in another solvent chloroform, the quality of the solvent or the solvent power did not increase in 30°-50°C range. The adsorption of styrene-butadiene copolymer also decreased with increasing temperature, and the phenomena was more marked in case of high molecular weight sample/153/. In most systems the increase in temperature have shown decrease in adsorption amount/25,89,154,156/.

Many workers /90,157,158/ have observed increase in adsorption amount with increase in temperature. The change in adsorption amount vary with different polymers and in some cases considerable changes are observed. Sometimes the temperature rise changes the flexibility of the polymeric chain and causes thermal deaggregation of the molecules so that they can penetrate more readily into the pores of the adsorbent.

The temperature coefficient of the same polymer can be different depending on the nature of the solvent and adsorbent. This was seen in the case of adsorption of poly(methyl methacrylate) on iron/154/, where a decrease was observed with increasing temperature. But the adsorption of the same polymer on glass from benzene did not change with increase in temperature between 30° to 70°C.

Hence it is clear that every system behaves in an independent manner making it difficult to generalize the overall adsorption behaviour with respect to temperature change. The effect of temperature variation on the extent of adsorption and the corresponding thermodynamics are discussed in this thesis.

1.8 THERMODYNAMIC PARAMETERS

Thermodynamics has acquired great significance in the study of chemical reactions, as all the chemical processes are accompanied with change in energy. It is applicable to all forms of the energy changes associated with physicochemical processess/159/. It is a science that deals with the macroscopic properties which might change in these systems.

The state of thermodynamic equilibrium in adsorption process on plane solid-liquid interface is characterized by the interfacial mass transfer which involves both adsorbed and solution species/160/. Solid-liquid partition of any solute will depend on thermodynamic factors. To correlate the thermodynamic functions characterizing the adsorption process with the characteristics of various systems is a challenging task in the study of physical chemistry of adsorption of polymers.

The thermodynamic description of the flexible macromolecular chains in solution and the experimentally established features of polymer adsorption are more complicated /161,162/ than that of low molecular weight substances. In fact surface coverage and interfacial exchanges are slow processess and polymer desorption, promoted by dilution of the suspension or by replacement of the liquid phase with pure solvent, are not generally observed. Thermodynamic Equilibrium is reached after a very long time.

The interfacial stability is generally attributed to the thermodynamic and kinetic properties of the adsorbed layer which are controlled by [i] the existence of multiple contact points between polymer and adsorbent/163,164/ [ii] the polymer entanglements in the diffuse zone constitute a kinetic limit to the polymer adsorption. It has been observed that desorption of polymer from the adsorbent surface is difficult/165/ even in presence of a good solvent. It has also been shown that this apparent irreversibility is not necessarily a true irreversibility, but a polydispersity effect /29/. The solid surface possesses a tendancy to assume minimum surface area so the attainment of equilibrium is a slow process. Cohen Stuart et al. /29/ proved beyond doubt that thermodynamic equilibrium in the polymer adsorption is reached which justifies the application of equilibrium thermodynamics to it. Models of adsorption have primarily been developed from free energy data. Entropy and enthalpy data might however be more sensitive to changes in adsorption behaviour because the free energies will result in part from compensating contributions from the entropy and enthalpy changes accompanying adsorption.

The various interactions existing in a three component system of polymer, adsorbent and solvent complicate the determination of enthalpy change associated with each of these interactions. Some of these can of course be determined by microcalorimetry /164-166,167/.

The equilibrium constant data obtained at various temperatures can be used to calculate the free energy of adsorption $\triangle G_{ads}$, and hence the entropy ΔS_{ads} and enthalpy ΔH_{ads} through thermodynamic approach. To compare the data for various systems a single reference state is preferable. The reference state chosen for this study was a hypothetical infinite 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°_{ads}, ΔS°_{ads} and ΔH°_{ads}. As these quantities are inherent characteristic of a system, they form a sound basis for comparative study.

1.9 VARIOUS PROPOSED THEORIES

The theoretical modelling of polymer adsorption has a long history and has been the subject of many reviews /168-174/. The theories developed at the initial stages had one thing in common, that in each case a partition function was formulated for the polymer molecule at the interface and the structure was calculated from a minimization of the free energy of the polymer. Such arguements helped in the calculation of the isotherms etc. The main difficulty was that a model of the polymer at an interface had to be constructed in order to facilitate the calculations, and the simplicity of the model were extreme to fit the results. Also the diversity in assumptions led to vastly different results.

Later theories/175,176/ included excluded volume interactions within a quasi-crystalline lattice model allowing calculations of site-site interactions through mean field approximations. Montecarlo simulations/177,178/ provided independent and mathematically exact results such as adsorbed layer thickness and fractional coverage of the surface.

Extension of the theoretical work to adsorption of multiple models/179-181/ resulted in the development of several lattice models. Among them the Scheutjens and Fleer model /182,182/ stands out describing many aspects of polymer adsorption, like the number of segments per chain and the polymer volume fraction in bulk solution etc. But the artificial approximations involved in selecting a particular lattice geometry and time consuming calculations limit its applications/184/.

The self consistant field theory developed by Edwards/185/ for polymer solutions was extended to adsorbing polymer by DiMarzio /171/ and DeGennes /186/. This was based on the fact that the statistics of polymer random walks are described by a diffusion equation /187,188/. This approximation has brought a variety of solution techniques and could be extended to important related problems. Ploehn et al. /184/ have formulated a general self consistant field model for polymer adsorption and considered the case of non ionic homopolymer adsorption at a single planar surface. Helfand /189,190/, Dickman and Hall /191/ developed a diffusion equation from statistical mechanical analysis modeling polymer-surface interaction as a 'sticky surface' by introducing new boundary conditions. The solution for the self consistent field theory has been obtained through a ground state approximation /192/ and an equation for the volume fraction profile of polymer segments has been derived/47/. This facilitated the calculation of total adsorbed amount of polymer, the fraction of segments in contact with the surface, the root mean square layer thickness and the hydrodynamic thickness.

Finally the computer simulations provided both a qualitative and quantitative means of understanding the factors influencing polymer-surface interactions/193,194/. 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, the 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 /195-200/ have described the computer simulation in detail for the homopolymers and copolymers, making the theoretical approach to polymer adsorption quite feasible.