STUDIES OF
ADSORPTION OF POLYMERS AND COPOLYMERS ON SOLID SURFACES

A SUMMARY OF THE THESIS
SUBMITTED TO
THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
(Chemistry)

By
ROYCHEN JOSEPH

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
M.S. UNIVERSITY OF BARODA, VADODARA

MAY 1992

SUMMARY

The work described in this thesis concentrates on the thermodynamics of the process of adsorption of homopolymers and copolymers on inorganic substrates, namely silica gel, alumina and calcium carbonate. The homopolymers were polybutadiene (PBR), poly(methyl acrylate) (PMA), poly(ethylacrylate)(PEA), poly(butyl acrylate)(PBA) and polyacrylonitrite (PAN).

Copolymers of acrylonitrile-methyl acrylate ($ANMA_{11}$, $ANMA_{12}$), acrylonitrile - ethylacrylate ($ANEA_{11}$, $ANEA_{12}$) and acrylonitrile - butylacrylate ($ANBA_{11}$, $ANBA_{12}$) chosen for the study were synthesized and characterized in the laboratory. The adsorption isotherms obtained at different temperatures were used for computing the thermodynamic parameters of adsorption. The thermodynamic quantities of adsorption of these polymers from infinitely dilute solutions, free energy ($\triangle G^0_{ads}$), enthalpy ($\triangle H^0_{ads}$) and entropy ($\triangle S^0_{ads}$) were computed and compared.

The homopolymers and copolymers were synthesized by solution polymerization technique using benzoyl peroxide (1% w/w) as intiator. The reaction conditions (85°C, 6 hours, DMF solvent) were identical for all systems. These polymers were thoroughly purified and characterized before using for the adsorption studies.

The characterization was done by elemental analysis, infrared spectroscopy (IR), ^{13}C NMR spectrosopy, differential scanning calorimetry (DSC),

differential thermal analysis (DTA), thermogravimetric analysis (TGA), contact angle studies and viscosity.

The copolymer composition were calculated from the elemental analysis (Nitrogen estimation) results. Thermal properties like glass transition temperature, decomposition temperature, activation energy of decomposition, thermal stability were elucidated by DTA, DSC and TGA. Contact angle studies showed that the surfaces of these copolymers were reasonably hydrophobic, with the critical surface tension values (γ_c) ranging from 37 to 21 mNm^{-1}. For higher homologous of acrylates and their increasing concentration γ_c values were found to decrease. The intrinsic viscosity $|\eta|$ decreased with increase in temperature. Using this data the viscosity average molecular weight $\overline{M}_v$ were computed for the homopolymers and copolymers. Voluminosity and shape factor calculated, showed that polymer molecules in the chosen solvents acquired spherical conformation at all the temperatures studied. .The activation parameters of viscous flow i.e. $\Delta G^{\ddagger}_{vis}$, $\Delta H^{\ddagger}_{vis}$ and $\Delta S^{\ddagger}_{vis}$ were also computed for these systems.

The adsorption of PBR was studied on alumina at different temperatures from cyclohexane (C), toluene (T) and three mixed solvent systems (80C:20T, 50C:50T, 20C:80T v/v). The adsorption isotherms for all these systems were similar. The specific adsorption showed the initial increase then a decrease and an increase before levelling off at higher concentrations. This was attributed to the effect of polydispersity, preferential adsorption of larger molecules and spreading of the adsorbed PBR on adsorbent surface. Specific adsorption was much higher from cyclohexane than from the other solvents. This decreased with the rise in temperature, as expected for an exothermic process.

Thermodynamic quantities of adsorption at infinite dilution ΔG^{o}_{ads}, ΔH^{o}_{ads} and ΔS^{o}_{ads} were computed from the initial linear rising part of the adsorption isotherms. ΔG^{o}_{ads} for all systems were negative indicating spontaneous adsorption process. This also signifies exothermic process of adsorption and loss in degree of randomness on adsorption. ΔG^{o}_{ads}, ΔH^{o}_{ads} and ΔS^{o}_{ads} when plotted against percentage solvent composition showed a slight maxima. It is known that there is unfavourable heat of mixing of cyclohexane and toluene, indicating that the mixture of above solvents was a better solvent for cis 1,4 polybutadiene, resulting in lower adsorption from mixed solvents than from pure solvent systems. Thus, the specific adsorption is definitely a function of solvent power.

Thermodynamic quantities were also calculated for each system as a function of surface coverage. The isosteric heat (ΔH_A) and entropy (ΔS_A), were negative and linearly decreased with the amount of PBR adsorbed for all solvent systems. The ΔH_o and ΔS_o calculated by this method were more negative than those calculated on the basis of extrapolation method, mentioned earlier. The plot of ΔH_o and ΔS_o against percentage composition of solvent mixtures showed the similar trend supporting the earlier conclusion.

The adsorption isotherms of polyacrylates (PMA, PEA and PBA) on alumina and $CaCO_3$ were of the usual Langmuir type. On silica gel the isotherms had a small semiplateau region. The nature of the isotherms were much different from those obtained for the PBR systems. This was due to the difference in the adsorbent - adsorbate interactions. The nature of the silica gel - polyacrylate isotherms were explained on the basis of the reasonably weak interaction between the surface hydroxyls of silica gel and the carbonyl group of the acrylates, which might lead to adsorption - desorption equilibrium. Other factors contributing to this effect were the multilayer formation and polydispersity.

The amount of polymer adsorbed decreased with the higher alkyl acrylates. This was attributed to the effect of bulkier side chains covering up the adsorbent sites. Also among the three adsorbents, specific adsorption was more on silica gel than alumina and least on $CaCO_3$. This was attributed to the effect of the surface area of the adsorbents. Silica gel containing more active sites accomodates more of the polymer. Surface areas of the alumina and $CaCO_3$ being less, a corresponding decrease in the amount adsorbed was seen.

The thermodynamic quantities $\triangle G^o_{ads}$, $\triangle H^o_{ads}$ and $\triangle S^o_{ads}$ were negative indicating an exothermic process of adsorption. These values were much lower for the $CaCO_3$ systems indicating weaker interaction between this adsorbent and the adsorbates, justifying the low specific adsorption.

Thermodynamic parameters obtained by the surface coverage approach also followed a similar pattern, but the magnitudes, as expected were different. These values also showed that the adsorption process was spontaneous and enthalpy dominated.

Adsorption isotherms of polyacrylonitrile on silica gel, alumina and $CaCO_3$ were of the usual Langmuir type. Specific adsorption was much higher than that of the polyacrylates and the copolymers. The higher molecular weight of PAN and smaller size of the nitrile moiety contributed to this effect. The semiplateau region was not observed for the silica gel - PAN system. This was because the interaction of the cyano group of PAN with the surface hydroxyls of silica gel was different than between the carbonyl group of the acrylates and silica gel - leading to an adsorption - desorption equilibrium in the latter case. The isotherm plateau was observed at a lower equilibrium concentration in comparison to polyacrylates and copolymers showing a certain difference in the characteristics of PAN vis a vis the other polymers.

The calculated thermodynamic quantities were higher for the PAN system than the other homopolymers and copolymers. These quantities were negative indicating an exothermic process of adsorption. Among the three adsorbents, these values were highest on silica gel than on alumina and the least on $CaCO_3$. Surface coverage approach also yielded similar values, but differing in magnitude.

The nature of the copolymer isotherms were similar to that obtained for the polyacrylates. Specific adsorption was in between the PAN and polyacrylates but nearer to that of polyacrylates. The specific adsorption decreased with the rise in temperature, increasing acrylate concentration and for higher homologoues of acrylates.

The thermodynamic quantities also followed a similar trend. These quantities showed that the copolymer composition had a marked influence in the adsorption process. The presence of higher alkyl acrylates and their increasing concentration decreased the specific adsorption and hence the thermodynamic quantities of adsorption i.e. free energy, enthalpy and entropy. Moreover, these quantities were much higher for the $ANMA_{11}$ systems on all the three adsorbents, supporting the above contention. In the copolymers of acrylonitrile with ethyl and butyl acrylate comonomer, the larger size of the side groups masked the effect of nitrile group.

The thermodynamic values obtained also support this view, where the values of $ANBA_{12}$ were more or less equal to the values of the butyl acrylate homopolymer. The thermodynamic values obtained by the surface coverage approach were also similar but higher in magnitude than the extrapolation method.

All the adsorption processes were exothermic, resulting in a lower specific adsorption at higher temperatures. Thermodynamic calculations showed that the heterogenity of the surface increased with temperature for all the systems. The adsorption process was an outcome of various interactions in the system like (i) solvent - polymer (ii) polymer - adsorbent (iii) adsorbent - solvent (iv) solvent - solvent and (v) polymer - polymer interactions. For all the systems the amount adsorbed was high on silica gel surface than alumina and least on $CaCO_3$. The polymer - silica gel interactions were stronger in all the systems.

The adsorption process showed a definite existence of compensation effect. The plot of ΔH^{0}_{ads} Vs ΔS^{0}_{ads} was linear for all the systems put together. This was found true for the two different thermodynamic approaches. The slope of the line yielded a constant temperature at which the adsorption process would be completely independent of entropic forces and would be governed by only enthalpic forces.

It could hence be concluded that reversible thermodynamics can be successfully applied to the adsorption of these homopolymers and copolymers on oxide substrates.