SUMMARY

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The work in this thesis is centered on thermodynamics of the adsorption process. The adsorption of synthetic and natural rubbers [synthetic polybutadiene (PBR) and natural rubbers obtained from Guyana (GR) and India (InR)] on silica gel and alumina was studied. These rubbers were also characterized. The adsorption of rubbers from various solutions at different temperatures, on alumina and silica gel, was carried out. The adsorption isotherms so obtained were then used for computing the thermodynamic quantities for adsorption. The free energy ΔG^o_{ads}, enthalpy ΔH^o_{ads}, and entropy ΔS^o_{ads} from infinitely dilute solution were then computed and compared. Solvents used were toluene, cyclohexane, and their mixtures for PBR and GR. For InR, solvents were toluene, chlorobenzene, and their mixtures. Cyclohexane was not used for InR because of the insolubility.

The characterization of the polymers was done by spectroscopic and thermal analysis, viscosity and contact angle studies. IR, NMR-^{13}C and PMR helped in the elucidation of the microstructure of rubbers. It was determined that PBR was cis-1,4 polybutadiene, GR was trans-1,4 polyisoprene, and InR was cis-1,4 polyisoprene. Intrinsic viscosity was different at different temperatures in different solvents, for each of the polymers. The plot of intrinsic viscosity against the solubility parameter of the solvent yielded the solubility parameter of the respective polymer. Voluminosity and shape factor calculated, showed that polymer molecules in chosen solvents acquired spherical conformations at all temperatures. The activation parameters of the viscous flow - $\Delta G^{\neq o}_{vis}$, $\Delta H^{\neq o}_{vis}$, and $\Delta S^{\neq o}_{vis}$ were different for different rubbers in various solvents.

Thermogravimetric analysis revealed different degradation patterns and thermal stability for PBR, GR and InR. Contact angle studies showed that the surfaces of these rubbers were very hydrophobic, as expected.

The adsorption of PBR was studied on silica gel at different temperatures, from cyclohexane [C], toluene [T] and various mixed solvent systems [80C:20T; 50C:50T; 20C:80T v/v]. The adsorption isotherms for all these systems were similar. They showed an initial increase in specific adsorption, a decrease, an increase thereafter before levelling off at higher concentrations. This was because 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 any other solvent systems. It decreased with increase in temperature, as expected for an exothermic adsorption process.

Various thermodynamic quantities of adsorption at inifinite 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, though that from mixed solvent system was relatively less so. All the ΔH^o_{ads} and ΔS^o_{ads} values were negative, though with different magnitudes indicating 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 maxima. This was due to unfavourable heat of mixing of cyclohexane and toluene, indicating that mixture of above liquids is a better solvent for cis-1,4 polybutadiene, resulting in least adsorption from mixed solvent than from pure solvent systems. Thus, the specific adsorption is definitely a function of solvent power.

Thermodynamic quantities were also calculated for each system for various surface coverage. The isosteric heat $[\triangle H_A]$ and entropy $[\triangle S_A]$, were negative, and linearly decreased with the amount of PBR adsorbed, for all solvent systems. The $\triangle H_0$ and $\triangle S_0$ calculated by this method were more negative than those calculated on basis of extrapolation method mentioned earlier. However, the similar trend was observed i.e. the $\triangle H_0$ and $\triangle S_0$ vs. percentage composition of solvent mixture plot showed maxima supporting the earlier conclusions.

The adsorption of GR was also studied at different temperatures, on alumina and silica gel, from cyclohexane, toluene and mixed solvents [50C:50T]. The isotherms obtained were of high affinity type and were much different from those obtained for PBR. The adsorption isotherms differ from the high affinity type, shown by Giles [H Type in Fig.1.4]. The difference is in the reasonably low adsorption obtained at low concentrations unlike the high adsorption expected from H Type isotherms. The isotherms are however very much similar to those observed by Cohen Stuart et al.(/105/). This showed that differences in chemical structure, microstructure, molecular weight, and MWD have a lot of influence on the overall adsorption process. Adsorption of GR from cyclohexane was much higher than from all other solvents, on both the adsorbents, as seen in PBR. This signifies that both PBR and GR systems behave somewhat similarly. A slight dip in the adsorption isotherm was observed for GR-toluene-alumina system at lower temperatures which then flattened to a semiplateau, at higher temperatures. This suggested the possibility of multilayer formation in polymer adsorption, besides the polydispersity effect. $\triangle G^o_{ads}$, $\triangle H^o_{ads}$, and $\triangle S^o_{ads}$ values though negative for all systems, were much less for mixed solvent

system. Therefore, the mixture of above liquids was a better solvent for trans-1,4 polyisoprene [GR] and hence least adsorption from this solvent. This was supported by viscosity study i.e. the intrinsic viscosity of mixed solvent was higher than pure solvent systems. We also observed that a discrepancy arises in defining a good solvent. The good solvent from viscosity point of view is not necessarily so from solubility parameter concept. This discrepancy was also observed earlier by other workers. The isosteric enthalpy and entropy linearly decreased with increase in the amount of GR adsorbed. The $\triangle H_0$ and $\triangle S_0$ values were negative for all systems but were higher for mixed solvent system, supporting the above contention.

The adsorption of InR was also studied at different temperatures, on silica gel and alumina, from toluene, chlorobenzene, and mixed solvents [80CB:20T; 50CB:50T; 20CB:80T v/v]. The adsorption isotherms obtained for InR-toluene on both the adsorbents, were of ladder type, unlike those observed for PBR and GR. The isotherms obtained for other systems were the conventional high affinity type. Thus the microstructure, conformational changes, molecular weight and MWD influence the overall adsorption process, as mentioned earlier. Ladder type isotherms suggested a definite multilayer adsorption. Adsorption from chlorobenzene was higher than from other solvent systems, on both the adsorbents. $\triangle G^o_{ads}$, $\triangle H^o_{ads}$, $\triangle S^o_{ads}$ though negative for all the systems, were much less negative for mixed solvent systems [i.e. relatively more positive]. The plot of $\triangle H^o_{ads}$ and $\triangle S^o_{ads}$ vs. percentage composition of toluene showed a maxima, for both the adsorbents. This suggested that mixed solvent system was better solvent for cis-1,4 polyisoprene, resulting in lower adsorption from this system.

Solubility parameter of chlorobenzene was 9.5 and that of toluene was 8.9. The intrinsic viscosity in toluene is higher than in chlorobenzene. Hence toluene seems to be a better solvent for lnR. The thermodynamic quantities for adsorption were more negative for silica gel than for alumina, suggesting the effect of polymer-adsorbent and adsorbent-solvent interactions on the overall adsorption process. The isosteric heat and entropy were also computed for different systems. The values were negative for all the systems.

All adsorption processes studied were exothermic, resulting in a lower specific adsorption at higher temperatures. Thermodynamic calculations showed that the heterogeneity of the surface increased with temperature, for all systems. The adsorption process was an outcome of various interactions in the system, like [1] polymer-solvent, [2] polymer-adsorbent, [3] adsorbent-solvent, [4] solvent-solvent, and [5] polymer-polymer interactions. For all the systems, amount of polymer adsorbed was much higher from poorer solvent system. The poor solvent being defined from the intrinsic viscosity data.

The adsorption on silica gel was slightly higher than on alumina, for all polymers from all solvent systems. This was because of comparable acidity of silica gel than alumina. The rubbers being Lewis base [electron pair donars because of the presence of double bonds] interacted to the same extent, with both the Lewis acids. The adsorption process therefore involves acid-base interactions. Tendency of higher adsorbent-solvent interaction resulted in competitive solvent adsorption, hence decreasing the amount of polymer adsorbed. The adsorption studies showed that though

adsorption on silica gel was higher, alumina also adsorbed sufficient amounts of PBR, GR and InR. Thus, besides commonly used silica gel, alumina could also be used as a filler in rubber industry. This is expected only on the basis of rubber-alumina interaction. Alumina as a reinforcing filler is of course a different aspect and has to be dealt separately.

The adsorption process showed a definite existence of compensation effect. The plot of $\triangle H^{o}_{ads}$ vs. $\triangle S^{o}_{ads}$ was linear for all the systems put together. This was true for two different thermodynamic approaches. The slope of the plot yielded a constant temperature at which the adsorption process is completely independent of entropic forces and is governed by only enthalpic forces.

Hence we conclude that reversible thermodynamics can be justifiably applied to the adsorption of natural and synthetic rubbers on oxide substrates. The results can be gainfully employed in understanding the polymer adsorption process.