The transport characteristics of macromolecular networks have been the object of active research for the past several years. A deep understanding of the intrinsic as well as extrinsic factors controlling the transport process through polymers is highly essential for fabricating suitable end products out of them, especially for those functioning in aggressive liquid environments.

This thesis presents the behaviour of natural rubber, one of the widely used elastomers, in presence of different liquids viz., aromatic, aliphatic and chlorinated hydrocarbons. The results have been explained in terms of different kinetic and thermodynamic parameters.
The transport behaviour of aromatic hydrocarbons through natural rubber vulcanized by four different systems viz., peroxide (DCP), conventional (CV), efficient (EV), and a mixture consisting of sulphur and peroxide (mixed) has been studied in detail. The sample crosslinked by using DCP showed the lowest equilibrium uptake value in all penetrants compared to the other samples. This has been explained in terms of the differences in the type of crosslinks formed between rubber chains during the four vulcanization techniques and also by the differences in crosslink density values. In a given system the maximum uptake value decreased with increase in molecular weight of the solvent. The interaction parameter values for the different systems indicated higher rubber-solvent interaction for the CV system than other systems.

The sorption and diffusion behaviour of aliphatic hydrocarbons through crosslinked NR has been found to be in good agreement with the experiments using aromatic hydrocarbons. The molecular weight between crosslinks, $M_c$, of rubber was found to vary significantly with the change of solvents. This has been explained in terms of the variations in rubber chain entanglement density in different solvents. The diffusion coefficient values showed an inverse dependence on the molecular weight of aliphatic hydrocarbons. Moreover, these values increased with rise in temperature which suggested the activation of diffusion process by temperature. This was in quantitative agreement with expectation. Of the four vulcanizing systems used the activation energy values were found to be higher for CV system indicating its higher temperature susceptibility.

The interaction of natural rubber with chlorinated hydrocarbons has been followed by a sorption (S)-desorption (D)-resorption (RS)-redesorption (RD)
technique. The mechanism of diffusion was found to be anomalous for sorption. However, the resorption mechanism followed the regular Fickian trend. The mechanical strength of the rubber samples was found to decrease significantly after establishing equilibrium in solvents. The stress-strain curves clearly indicated the absence of strain induced crystallisation in the swollen specimens. The modulus of a given sample was found to be different in different solvents. This has been explained in terms of the differences in the contribution of physical entanglements to the total crosslink density.

Since carbon black is extensively used for rubber reinforcement, the influence of carbon black particles of different size on the transport characteristics of NR has been systematically analysed. The solvent uptake followed the order semireinforcing furnace > high-abrasion furnace > intermediate super-abrasion furnace > super-abrasion furnace loaded NR samples. The reason for this trend has been attributed to the increased restriction to the overall chain mobility and flexibility of polysulphidic linkages with decrease in the size of carbon black particles. The diffusion coefficient values, determined by considering the isotropic swelling in the samples, decreased with decrease in the size of the reinforcement. The activation energy values were found to be highest for semireinforcing furnace loaded samples indicating their highest temperature susceptibility.

The liquid sorption behaviour of NR loaded with carbon black (HAF) and that with silica (ultrasil VN3) of same loading has been compared. It was found that the black incorporated samples sorb lesser amount of aromatic solvents compared to the silica filled ones. This has been explained in terms of the high bound rubber content and crosslink density of black filled vulcanizates due to
high rubber-filler interaction. Mechanism of transport in both black and silica loaded NR samples, was found to follow an anomalous trend as indicated by the deviation from the theoretical curves describing Fickian transport. The transport coefficients have been observed to vary inversely with both cure time of rubber and penetrant molecular size. The calculated thermodynamic functions indicated higher rubber-solvent interaction in silica filled samples than the black loaded ones and supported the observation of decrease in equilibrium sorption values with both cure time of rubber and molecular size of the penetrants.

Finally, the feasibility of a pervaporation technique for the separation of organic liquid mixtures using natural rubber membranes vulcanized by different techniques has been examined. It was observed that the membranes exhibit permselectivity towards aliphatic hydrocarbons and chlorinated hydrocarbons from their mixtures with acetone. Of the four vulcanizing systems, the membrane vulcanized by DCP exhibited highest separation efficiency. The separation efficiency was found to decrease with increase in cure time of the membranes. The selectivity of the membranes appeared to be independent of their thickness but the flux decreased with increase in membrane thickness.