CHAPTER VII

SUMMARY

VII.A SUMMARY

Recently, thermoplastic polymers have played an important role as barrier materials in industrial, biological, pharmaceutical and engineering areas as well as in tackling the environmental pollution problems. For successful applications of these materials, it is necessary to have a detailed knowledge of the mechanism of solvent transport into the barrier membranes. However, the molecular transport of liquids into polymer membranes has been studied both theoretically and experimentally. The transport phenomenon is dependent upon the polymer structure and its interactions with the organic liquids. It is therefore important that for many applications of the membrane materials, an understanding of the polymer-solvent interactions, in addition to polymer swelling, is necessary.

An important requirement of a membrane in any application area is that it should be chemically resistant and it should retain the mechanical properties and dimensional stability under prolonged exposure to liquids. However, the molecular transport of organic liquids into polymer membranes under the influence of chemical potential gradient takes place by a sorption/desorption and diffusion mechanisms. In order to judge the suitability of a membrane material for any specific application, it is
important to evaluate sorption, desorption and diffusion coefficients. A study of the concentration dependence of these parameters is a formidable task theoretically, nevertheless empirical formulae have been developed.

Innumerable research efforts have been made to study the experimental and theoretical aspects of molecular transport phenomenon. In the present thesis, empirical and theoretical approaches have been used to study the polymer-solvent interactions and to estimate the sorption and diffusion parameters in order to assess the usefulness of the membranes used under extreme service conditions. The polymers used in this study are: (i) tetrafluoroethylene/propylene copolymers Aflas™ (FA 100S and FA 150P) and Fluorel® (FC-2179 and FLS-2650) fluoroelastomers, 3M Company, (USA) and (ii) Du Pont's VITON fluoroelastomers. The organic probe liquids used are: (i) alkanes and hydrocarbon, (ii) chloroalkanes, (iii) esters, (iv) ketones and nitriles, (v) aromatics and (vi) dipolar aprotic liquids. The sorption/desorption parameters have been measured by using the gravimetric weight-gain method at 30, 45 and 60°C for fluoropolymer membranes and for VITONs at 25, 44 and 60°C. However, with some liquids having low boiling points, the upper temperature limit used was 50°C. For VITONs, the sorption (S), desorption (D), resorption (RS) and redesorption (RD) i.e., S-D-RS-RD experiments were performed at 25°C. With Aflas™ and Fluorel® elastomers, only sorption experiments were performed. Such a data-base on the type of polymers and solvents used are not available previously in the literature. Therefore, the present investigation is undertaken. The thesis is divided into six major chapters in addition to a summary chapter as the seventh chapter.
The first chapter deals with the discussion of literature data on various polymer-solvent systems that are relevant to the present study. Only the representative references are covered. Second chapter describes the experimental details and the techniques used. The chemistry, technology and fabrication of the polymers used along with their chemical/mechanical properties are presented. Details of the gravimetric weight-gain method and the computational procedures are discussed. A brief account is also given about the choice of the solvents along with their importance in related industries.

Third chapter deals with the sorption testing of esters, ketones and nitriles into two Aflas™ FA 100S and FA 150P copolymer membranes. Solvents: (i) esters: methyl acetate, ethyl acetate, \( n \)-propyl acetate, \( n \)-butyl acetate, \( iso \)-amyl acetate, diethyl oxalate, diethyl malonate, methyl benzoate, methyl salicylate and ethyl benzoate and (ii) ketones and nitriles: acetone, methyl ethyl ketone, cyclohexanone, methyl \( iso \)-butyl ketone, acetonitrile and acrylonitrile are employed. Sorption results at 30, 45 and 60°C are obtained to calculate the diffusion and permeation coefficients from Fick's equation. The dependence of transport parameters along with kinetic rate constants on the size, shape and nature of the solvents has been discussed. Concentration profiles of the liquids inside the membranes at different penetration depths have been obtained and compared with those obtained from the analytical solutions of Fick's equation.

Fourth chapter covers a discussion on sorption kinetics of alkanes, chloroalkanes and dipolar aprotic liquids into two Aflas™ FA 100S and FA
150P copolymer membranes. Solvents used are: (i) **alkanes and hydrocarbon**: hexane, cyclohexane, heptane, octane, 2,2,4-trimethylpentane, nonane and decane, (ii) **chloroalkanes**: dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene and tetrachloroethylene and (iii) **dipolar aprotic liquids**: tetrahydrofuran, 1,4-dioxane and dimethylacetamide. Also, sorption kinetics of aromatic liquids such as benzene, toluene, mesitylene, methoxybenzene, chlorobenzene, bromobenzene and 1,2-dichlorobenzene into Aflas™ FA 150P fluoropolymer membranes have been studied. The coefficients of sorption, diffusion and permeation are calculated using Fick's equation. These results have been discussed on the basis of molar volumes, dipole moments and concentration profiles of the probe molecules.

In the fifth chapter, transport results for ketones, nitriles, esters, chloroalkanes, aromatics and dipolar aprotic liquids into two Fluorel® FC-2179 and FLS-2650 fluoroelastomers are presented. Liquids selected and the methods used to analyze the transport results are the same as those given in Chapters III and IV. Numerical techniques based on the finite difference method have been employed to obtain the liquid concentration profiles and these are compared with those obtained from the analytical solutions of Fick's equation. Concentration dependency of diffusion is also investigated in some cases.

In the sixth chapter, the S-D-RS-RD testing of ketones, nitriles and dipolar aprotic liquids into three VITON fluoropolymers has been studied. Experiments have been conducted at 25, 44 and 60°C. The ketones and
nitriles selected are the same as given in Chapter V. Dipolar aprotic liquids viz., dimethyl sulfoxide, dimethylformamide, tetrahydrofuran, 1,4-dioxane and dimethylacetamide were selected for the S-D-RS-RD testing. Transport results of dimethyl sulfoxide, 1,4-dioxane and toluene into four isocyanate samplers (VITON 5507, 5508, 5509 and 5510) are presented. It is found that the transport coefficients depend on the nature of liquids instead of their molecular sizes.

In summary, the results of this investigation will add a wealth of new information regarding transport phenomenon. Also, it will be a good contribution to the literature of membrane science. This data-base will have immense value to polymer scientists and technologists for a better selection of the materials to a specific application. Some of the problems which could not be addressed in this research may be extended further by using a more sophisticated instrumentation such as capillary column inverse gas chromatography (CCIGC) for estimating diffusion coefficients and for studying accurately the polymer-solvent interactions. The Cahn microbalance may be used for the study of the low sorbing liquids. The use of both these techniques will add a wealth of new information on the solvent transport properties. Some of these approaches will be attempted in the near future as an extension of this problem.