SUMMARY
The present investigations have been carried out to study the transport properties of ethylene glycol, diethylene glycol and their aqueous solutions through some inorganic membranes namely titanium oxide, zirconium oxide and antimony oxide. The results obtained have been analysed in the light of the theory of non-equilibrium thermodynamics. The work reported in the thesis has been summarised below:

In chapter I, a brief description of natural and artificial membranes has been given. Different types of membranes have been discussed with a special reference to synthetic ion-exchange membranes. Artificial inorganic ion-exchange membranes have been discussed in detail. A review of transport studies through inorganic membranes in recent years has been included in this chapter. The objectives of present investigations have also been given.

A brief discussion of the theory of non-equilibrium thermodynamics of irreversible processes has been given in chapter II. A detailed description of electro-kinetic phenomena in linear and non-linear range has been given.

Hydrodynamic permeability of ethylene glycol, diethylene glycol and their aqueous mixtures has been measured and the results obtained are in accordance with the theory of non-equilibrium thermodynamics. The values of phenomenological coefficient decrease as the composition of ethylene glycol and
diethylene glycol increases in water. These trends are consistent with the structural modifications that occur in EG-water or DEG-water mixtures because of hydrogen bonding.

The frictional coefficient, $f_{\omega m}$, between water and membrane has been evaluated for each membrane. The order of variation of $f_{\omega m}$ is in conformity with the order observed that for phenomenological coefficient $L_{22}$. The variation of $f_{\omega m}$ with the composition of EG and DEG in water has been found to be non-linear. This has been attributed to the formation of an associated complex due to hydrogen bonding as the concentration of EG or DEG in water goes on increasing.

The molecular exchange rate $K_{p\alpha}$ between the two phases of the membrane has been evaluated for different compositions of ethylene glycol and diethylene glycol in water across each membrane from the statistical theory of transport processes. The values of $K_{p\alpha}$ for different compositions across each membrane suggest that the transport through membranes follows the activated unit rate process.

The concentration dependence of phenomenological coefficients, $L_{22}$, has not been found to be in accordance with the Speigler's model. The variation of coefficient $L_{22}$ has been observed to be non-linear. This has been attributed to the formation of an associated complex of EG-$H_2O$ and DEG-$H_2O$ in liquid state which may prevent the linear behaviour of $L_{22}$ with varying composition of EG and DEG in water.
The variation of phenomenological coefficient, $L_{22}$, with temperature has different compositions of ethylene glycol and diethylene glycol in water across each membrane has been observed in accordance with the expression:

$$\log L_{22} = K - \frac{E_\eta}{kT}$$

(5.1)

where $K$ is a constant and $E_\eta$ is the energy of the activation.

Activation energy parameters viz. enthalpy of activation ($\Delta H^*$), entropy of activation ($\Delta S^*$) and free energy of activation ($\Delta G^*$) have been evaluated for different compositions of ethylene glycol and diethylene glycol in water across each membrane from the knowledge of hydrodynamic permeability at different temperatures. It has been observed that the entropy of activation ($\Delta S^*$) for different systems across each membrane decreases with the increasing viscosity. The decrease has been observed to be more rapid in case of the medium containing DEG. This has been attributed to the greater interactions of the medium containing DEG with the membrane. The decrease in $\Delta S^*$ with increasing viscosity of the medium has been observed to be maximum in case of zirconium oxide membrane. This has been attributed to the stronger interactions of the medium containing EG and DEG with membrane matrix. The values of $\Delta G^*$ for all the cases studied have been found to be positive. This shows that the flow across the membranes is not favoured i.e. it just can not
take place unless an external force (like pressure in present case) is applied across the membrane.

The electro-osmotic permeability of different compositions of ethylene glycol, and diethylene glycol in water has been measured across each membrane and the results obtained are in accordance with the theory of non-equilibrium thermodynamics. All membranes have been characterised in terms of pore radii, number of pores and zeta-potential. The characterisation of membranes has been done in light of the capillary model. For all the system studied across each membrane, it has been observed that the pore radius increases with the decrease in the water contents of the mixtures containing ethylene glycol, and diethylene glycol. This has been attributed to the swelling of the membrane with varying composition of water in the permeant. Since the swelling is more in case of solvent with higher dielectric constant, the increase in pore radius with decreasing dielectric constant is well understood. The number of pores that theoretically make up the membrane has not been found to be constant for all the system studied across each membrane.

For a particular membrane, the value of zeta potential goes on increasing with increasing concentration of EG and DEG in water. This has been attributed to the increase in the thickness of the electrical double layer because of decrease
in autoprotolysis due to positive inductive effect on moving from lower concentration of EG and DEG towards higher concentration in water.

The concentration dependence of the phenomenological coefficient, $L_{21}$, has also not been found in accordance with Speigler's model of frictional forces. This has also been attributed to the formation of an associated complex between EG-water and DEG-water in liquid state due to hydrogen bonding.

The efficiency of energy conversion in case of electro-osmosis has been studied across each membrane and the results obtained are in accordance with the theory of non-equilibrium thermodynamics.

Second order phenomenological coefficients owing to the non-validity of linear phenomenological relations have been estimated in present investigations from the data of electro-osmosis and electro-osmotic pressure difference. The variation of second-order phenomenological coefficients has been explained on the basis of dielectric constant of the permeant. It has been found that the range of validity of linear relations increases with decreasing dielectric constant of the permeant. The variation of second-order phenomenological coefficients has also been explained on the basis of electrical double layer theory.
To analyse the dependence of the second-order phenomenological coefficients on the composition of the mixtures further, kinetic interpretation of the second order phenomenological coefficients, in terms of known physical parameters of the system has been employed. It has been observed that the second order phenomenological coefficients are the functions of the physical properties of the permeant and membrane characteristics like pore radius, number of pores and zeta-potential of solid-liquid interface. This conclusion has further been supported on the basis of electrical-double layer theory.