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Ion transport studies through polystyrene based model membrane: Conductance data and absolute reaction rate theory

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ABSTRACT

Conductances of polystyrene based nickel phosphate membrane prepared at applied pressure (P4T) bathed in Lithium, sodium and potassium chloride solutions of different concentrations and at different temperatures have been measured. Absolute reaction rate theory has been applied to derive various thermodynamic parameters, Ea, $\Delta H^{\neq}$, $\Delta F^{\neq}$ *and* $\Delta S^{\neq}$. *The interionic jump distance (d) has also been evaluated and found to be* $1.6A^{0}$. *The activation energies are found to depend on the site of penetrant species and decrease with the increase in the concentration of the bathing solutions. It is concluded that the membrane is weakly charged and ionic species retain their hydration shell, at least partially, while diffusing through the membrane pores. The values of* $\Delta s^{\neq}$ *are negative indicating, that partial immobilization of ions takes place probably due to the interstitial permeation and ionic interaction with the fixed charge groups of the membrane skeleton. Scanning Electron Microscope (SEM) images of the membrane have also been presented.*

Keywords: Nickel phosphate membrane, Activation energies, membrane conductance, thermodynamic parameters, SEM Micrograph.

INTRODUCTION

Since membranes of biological origin are complexes and not always easily reproducible, a number of researches have used model systems for carrying out their studies of structure and dynamics of biomembrane systems (1,2). Parchment membrane behave exactly like gestric mucosal membrane (3). In this paper we describe the application of absolute reaction rate theory to the membrane conductance data at different temperatures for investigating the mechanism of ion transport and the evaluation of interionic jump distance through polystyrene based nickel phosphate membrane.

MATERIALS AND METHODS

Preparation of membrane:

The polystyrene based nickel phosphate membrane was prepared by the method suggested by Beg and Coworkers (4). Nickel phosphate precipitate was prepared by mixing a 0.2M nickel (II) chloride with 0.2M tri-sodium phosphate solution. The precipitate was washed well with deionized water to remove free electrolyte and dried at room temperature. The precipitate was ground into fine powder and was sieved through 200 mesh (granule size 0.07 mm). Pure amorphous polystyrene (cross linked with1% 81535) were also grounded and sieved. Different proportions of polystyrene and nickel phosphate precipitate were mixed thoroughly using grinder. The mixture was then kept into the cast die having diameter 2.45 cm and place in an oven maintained at 200^0C for about half an hour to equilibrate. The die containing the mixture was then transferred swiftly to a pressure device (Spectra Lab., Model SL 89, UK) and pressures such as 4T was applied during the formation of the membrane. As a result nickel phosphate membranes of approximate thickness 0.095 cm was obtained. Our effort was to get the membrane of adequate chemical and mechanical stability. Thus, the membranes prepared by mixing 25% of polystyrene was found to be mechanically stable and was quite suitable for our studies. Those containing larger amount (> 25%) of polystyrene did not give reproducible results, while those containing lesser amount (<25%) were unstable. The total amount of the mixture, thus, utilized for the preparation of the membrane contained 0.125 g of polystyrene and 0.0375 g of nickel phosphate.

Measurement of membrane conductance:

The membrane was sealed between two half cells. The half cells were first filled with electrolyte solutions (KCl, NaCl or LiCl) to equilibrate the membrane (Fig. 1). The solutions wee replaced by purified mercury without removing the adhering surface liquids. The trapped air, if any, was removed from the membrane-solution interface in order to get reproducible results. Platinum electrodes were used to establish electrical contacts. The membrane conductance were monitored on a direct reading conductivity meter 303 (Systronics) at a frequency of 10^3 Hz. All measurements were carried at 25^0, 30^0, 35^0,40^0, 45^0 and 50^0 (+0.1^0C). The electrolyte solutions were prepared from AR reagents in deionized water.

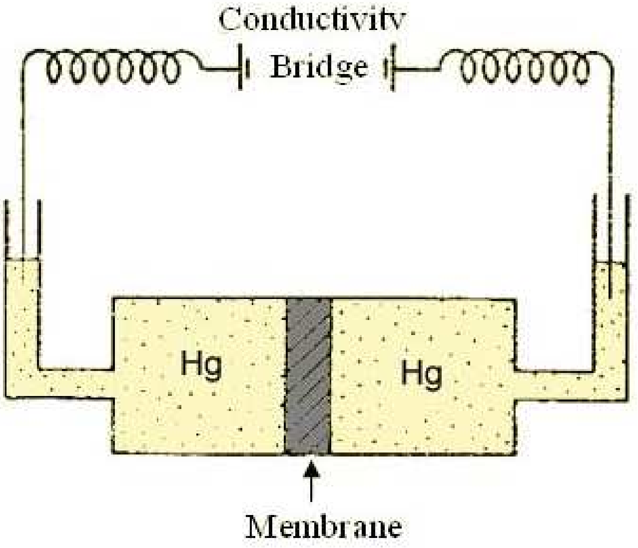

Fig. 1 Cell for measuring electrical conductivity of membrane

SEM investigation of membrane morphology :

Recently, a number of investigators while developing precipitates or membranes / thin film have frequently utilized scanning electron microscope (SEM) micrographs for their characterization (5-7). The composite pore structure, micro/macro porosity, homogeneity, thickness, cracks and surface texture/morphology have been specially studied by scanning electron microscopy (8-10). The information obtained from microscopic photographs/image have provided guidance in the preparation of well ordered precipitates and/or crack-free membranes. Consequently, the SEM surface images of the nickel phosphate membranes were taken. These are presented in Fig. 2. SEM images appear to be composed of dense and loose aggregation of small particles and formed pores probably with non-linear channel but not fully interconnected. Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various size.

RESULTS AND DISCUSSION

The conductance of polystyrene based nickel phosphate membrane bathed in potassium, lithium and sodium chloride solutions of different concentrations measured at different temperatures are given in Table (1-6) and are plotted in Figs. (3-5). These data show that the specific conductance of the membrane increases with increase in the concentration of the electrolyte and attains a maximum limiting value. This is in accordance with the findings of Iijima et al. (11) for nylon membranes with various alkali chlorides. The sequence of membrane conductance for the alkali metal ions under the same condition is $K^+ > Na^+ > Li^+$, similar to their ionic radii order. Similar behaviour was observed by several investigators for certain organic membranes (12-17). This sequence indicates that the size of the ions is the major factor in the diffusion process. Membrane porosity in relation to the size of the species (hydrated) flowing through the membrane seems to determine the above sequence. Although the sizes of the hydrated electrolytes are not known with certainty, there are few tabulations (18,19) of the number of mol of water associated with some electrolyte.

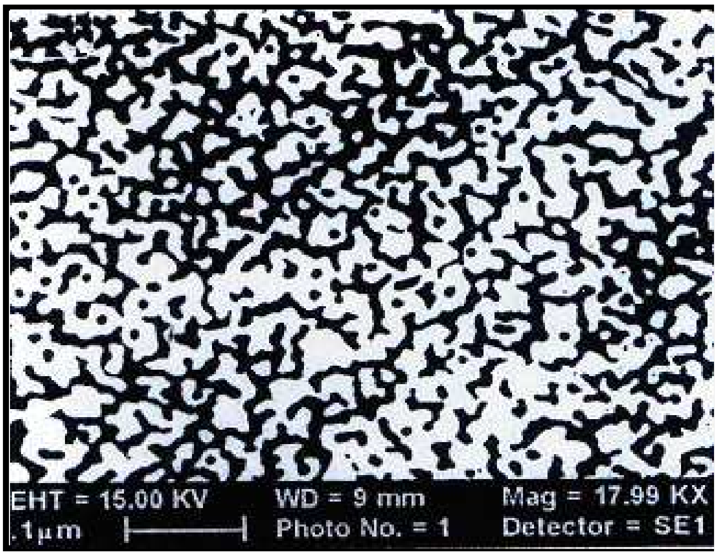

Fig. 2 SEM image of polystyrene based (25%) nickel phosphate membrane prepared at applied pressure (P4T).

Table 1 Observed values of specific conductance (m. ohm^{-1} Cm.$^{-1}$) through polystyrene based nickel phosphate membrane prepared at applied pressure (P4T) for 1:1 electrolytes at 25±0.1^{0}C

Membrane Electrolyte Concentration (M)	Nickel Phosphate		
	KCl	NaCl	LiCl
0.1/0.1	8.7×10^{-2}	7.1×10^{-2}	6.7×10^{-2}
0.05/0.05	5.3×10^{-2}	4.4×10^{-2}	3.9×10^{-2}
0.2/0.02	2.7×10^{-2}	2.2×10^{-2}	2.1×10^{-2}
0.01/0.01	2.5×10^{-2}	2.2×10^{-2}	1.7×10^{-2}
0.005/0.005	1.8×10^{-2}	1.3×10^{-2}	1.1×10^{-2}
0.002/0.002	1.3×10^{-2}	1.2×10^{-2}	1.1×10^{-2}
0.001/0.001	0.8×10^{-2}	0.8×10^{-2}	0.7×10^{-2}

Table 2 Observed values of specific conductance (m. ohm^{-1} Cm.$^{-1}$) through polystyrene based nickel phosphate membrane prepared at applied pressure (P4T) for 1:1 electrolytes at 30±0.1^{0}C

Membrane Electrolyte Concentration (M)	Nickel Phosphate		
	KCl	NaCl	LiCl
0.1/0.1	9.5×10^{-2}	7.1×10^{-2}	6.5×10^{-2}
0.05/0.05	7.8×10^{-2}	6.1×10^{-2}	5.7×10^{-2}
0.2/0.02	5.7×10^{-2}	4.7×10^{-2}	3.9×10^{-2}
0.01/0.01	3.7×10^{-2}	2.9×10^{-2}	2.9×10^{-2}
0.005/0.005	2.7×10^{-2}	2.5×10^{-2}	1.9×10^{-2}
0.002/0.002	1.7×10^{-2}	1.7×10^{-2}	1.6×10^{-2}
0.001/0.001	1.1×10^{-2}	0.9×10^{-2}	0.9×10^{-2}

Table 3 Observed values of specific conductance (m. ohm^{-1} Cm.$^{-1}$) through polystyrene based nickel phosphate membrane prepared at applied pressure (P4T) for 1:1 electrolytes at 35±0.1^{0}C

Membrane Electrolyte Concentration (M)	Nickel Phosphate		
	KCl	NaCl	LiCl
0.1/0.1	10.4 x 10^{-2}	7.9 x 10^{-2}	7.2 x 10^{-2}
0.05/0.05	8.1 x 10^{-2}	7.0 x 10^{-2}	6.3 x 10^{-2}
0.2/0.02	7.1 x 10^{-2}	5.3 x 10^{-2}	4.8 x 10^{-2}
0.01/0.01	4.7 x 10^{-2}	3.3 x 10^{-2}	3.1 x 10^{-2}
0.005/0.005	3.7 x 10^{-2}	2.7 x 10^{-2}	2.4 x 10^{-2}
0.002/0.002	2.7 x 10^{-2}	1.8 x 10^{-2}	1.8 x 10^{-2}
0.001/0.001	1.6 x 10^{-2}	1.1 x 10^{-2}	0.9 x 10^{-2}

Table 4 Observed values of specific conductance (m. ohm^{-1} Cm.$^{-1}$) through polystyrene based nickel phosphate membrane prepared at applied pressure (P4T) for 1:1 electrolytes at 40±0.1^{0}C

Membrane Electrolyte Concentration (M)	Nickel Phosphate		
	KCl	NaCl	LiCl
0.1/0.1	11.9 x 10^{-2}	9.3 x 10^{-2}	7.7 x 10^{-2}
0.05/0.05	10.7 x 10^{-2}	8.1 x 10^{-2}	7.1 x 10^{-2}
0.2/0.02	8.6 x 10^{-2}	6.1 x 10^{-2}	5.1 x 10^{-2}
0.01/0.01	5.7 x 10^{-2}	4.1 x 10^{-2}	3.5 x 10^{-2}
0.005/0.005	4.9 x 10^{-2}	2.9 x 10^{-2}	2.7 x 10^{-2}
0.002/0.002	2.9 x 10^{-2}	1.9 x 10^{-2}	1.9 x 10^{-2}
0.001/0.001	1.9 x 10^{-2}	1.4 x 10^{-2}	1.1 x 10^{-2}

Table 5 Observed values of specific conductance (m. ohm^{-1} Cm.$^{-1}$) through polystyrene based nickel phosphate membrane prepared at applied pressure (P4T) for 1:1 electrolytes at 45±0.1^{0}C

Membrane Electrolyte Concentration (M)	Nickel Phosphate		
	KCl	NaCl	LiCl
0.1/0.1	12.7 x 10^{-2}	10.9 x 10^{-2}	8.7 x 10^{-2}
0.05/0.05	11.7 x 10^{-2}	9.3 x 10^{-2}	8.1 x 10^{-2}
0.2/0.02	9.7 x 10^{-2}	6.7 x 10^{-2}	5.1 x 10^{-2}
0.01/0.01	6.6 x 10^{-2}	5.3 x 10^{-2}	4.1 x 10^{-2}
0.005/0.005	4.5 x 10^{-2}	3.9 x 10^{-2}	3.0 x 10^{-2}
0.002/0.002	3.3 x 10^{-2}	2.3 x 10^{-2}	2.3 x 10^{-2}
0.001/0.001	1.7 x 10^{-2}	1.1 x 10^{-2}	1.4 x 10^{-2}

Table 6 Observed values of specific conductance (m. ohm^{-1} Cm.$^{-1}$) through polystyrene based nickel phosphate membrane prepared at applied pressure (P4T) for 1:1 electrolytes at 50±0.1^{0}C

Membrane Electrolyte Concentration (M)	Nickel Phosphate		
	KCl	NaCl	LiCl
0.1/0.1	13.9 x 10^{-2}	11.3 x 10^{-2}	9.7 x 10^{-2}
0.05/0.05	13.2 x 10^{-2}	10.5 x 10^{-2}	8.9 x 10^{-2}
0.2/0.02	10.7 x 10^{-2}	8.1 x 10^{-2}	6.4 x 10^{-2}
0.01/0.01	7.1 x 10^{-2}	5.3 x 10^{-2}	4.1 x 10^{-2}
0.005/0.005	5.1 x 10^{-2}	4.1 x 10^{-2}	3.3 x 10^{-2}
0.002/0.002	3.7 x 10^{-2}	2.5 x 10^{-2}	2.4 x 10^{-2}
0.001/0.001	2.1 x 10^{-2}	1.2 x 10^{-2}	1.7 x 10^{-2}

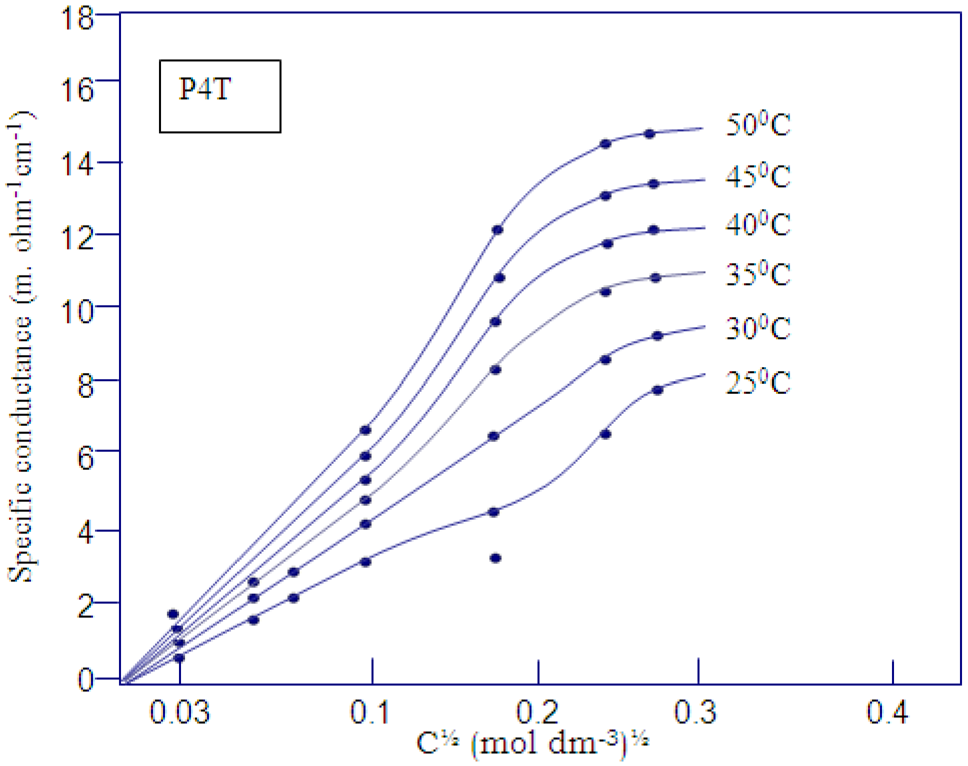

Fig. 3 Plots of specific conductance (m ohm^{-1} cm^{-1}) against square root of concentrations (mol dm^{-3})^{½} for KCl at different temperatures through polystyrene based nickel phosphate membrane prepared at applied pressure (P4T).

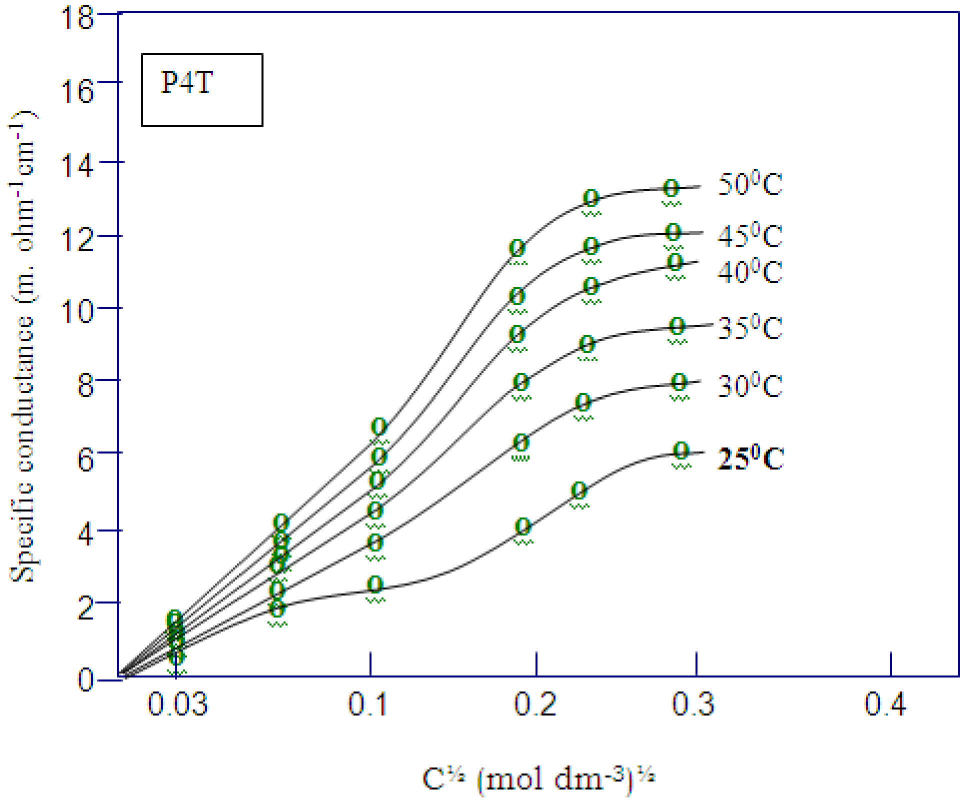

Fig. 4 Plots of specific conductance (m ohm^{-1} cm^{-1}) against square root of concentrations (mol dm^{-3})^{½} for NaCl at different temperatures through polystyrene based nickel phosphate membrane prepared at applied pressure (P4T).

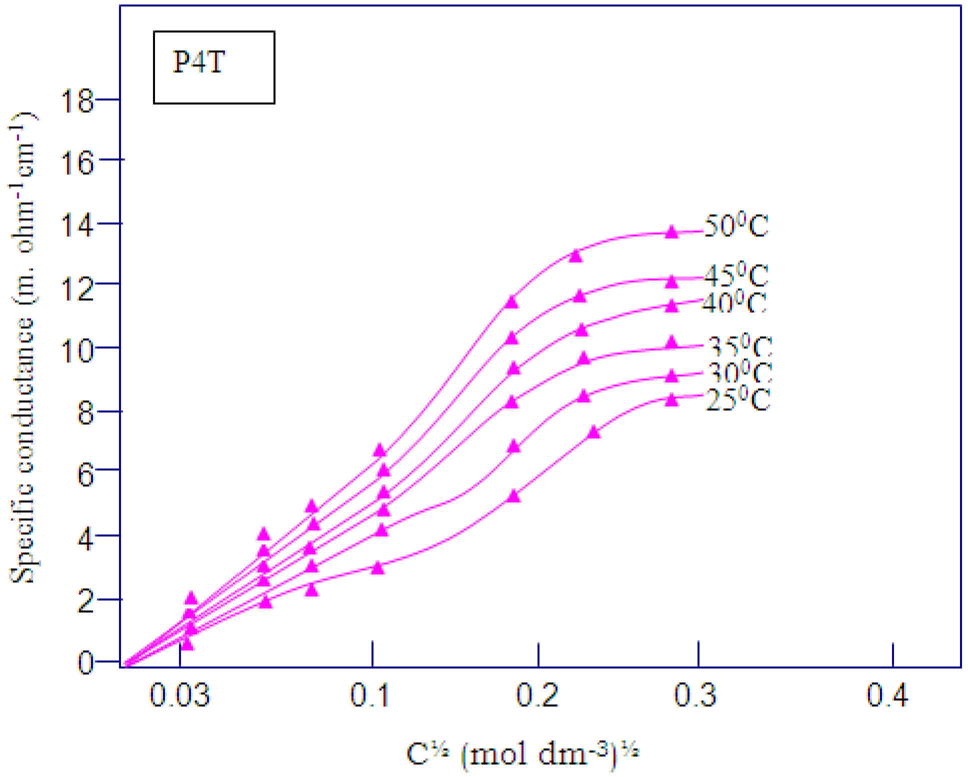

Fig. 5 Plots of specific conductance (m ohm^{-1} cm^{-1}) against square root of concentrations (mol dm^{-3})^{½} for LiCl at different temperatures through polystyrene based nickel phosphate membrane prepared at applied pressure (P4T).

Table-7 Values of thermodynamic parameters for polystyrene based nickel phosphate membrane prepared at applied pressure (P4T) in contact with different concentration of various 1:1 electrolyte solutions

Electrolyte conc. (mol. dm^{-3})	**Parameters**			
	E_a **(k Joule mol^{-1})**	$\Delta H^{\neq}$ **(k Joule mol^{-1})**	$\Delta F^{\neq}$ **(k Joule mol^{-1})**	$\Delta S^{\neq}$ **(k Joule mol^{-1})**
KCl				
0.1	10.2	6.8	73.6	-222.6
0.01	13.3	7.8	77.2	-232.3
0.001	15.7	11.7	81.3	-232.1
0.0001	20.7	16.1	85.7	-232.1
NaCl				
0.1	9.2	6.3	72.6	-223.5
0.01	12.6	6.7	74.1	-226.2
0.001	13.7	11.4	79.3	-226.8
0.0001	19.1	12.3	82.8	-236.4
LiCl				
0.1	9.2	5.7	73.6	-227.2
0.01	12.3	7.1	74.6	-225.8
0.001	13.6	11.1	80.8	-235.3
0.0001	18.0	8.2	79.5	-235.6

However, in Fig. 6 a plot of specific conductance of different electrolytes (chlorides) against free energy of hydration of cation (20) is given for the membrane. It is seen that specific conductance decreases with increasing hydration energy, i.e. greater size due to increase in hydration. This points to the fact that the electrolyte is diffusing along pores or channels of dimensions adequate to allow the substance to penetrate the membrane. The state of hydration of the penetrating electrolyte may be considered to exist in a dynamic condition so that at higher temperatures considerably higher fraction of the total number of given kind would possess excess energy (ΔE) per mol according to the Boltzmann distribution $f = e^{-\Delta E/RT}$ (R is the gas constant). Under these circumstances, those ionic species which have lost sufficient water of hydration and thus are smaller is size than the size of the pore would enter of membrane. This way the specific conductance would increase with increase in temperature, provided the membrane has undergone no irreversible change in its structure. That no such structural change involved is evident from the linear plots of log in versus 1/T shown in Fig. 7, the slope of which gives the energy of activation as required by Arrhenius equation.

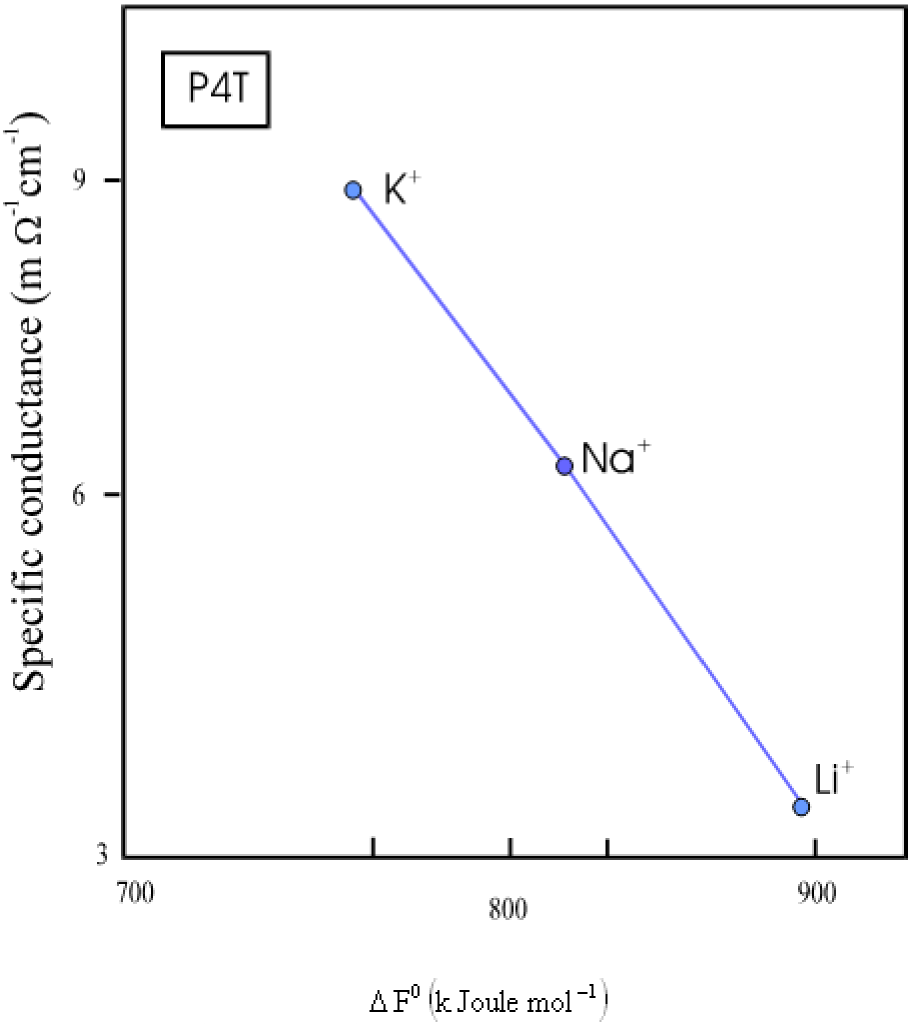

Fig. 6 Specific conductance $(m\ \Omega^{-1}cm^{-1})$ of various 1:1 electrolytes at 25^{0}C through polystyrene based nickel phosphate membrane prepared at applied pressure (P4T) plotted against the free energy of hydration, F^0, (k Joule mol^{-1}) of cations.

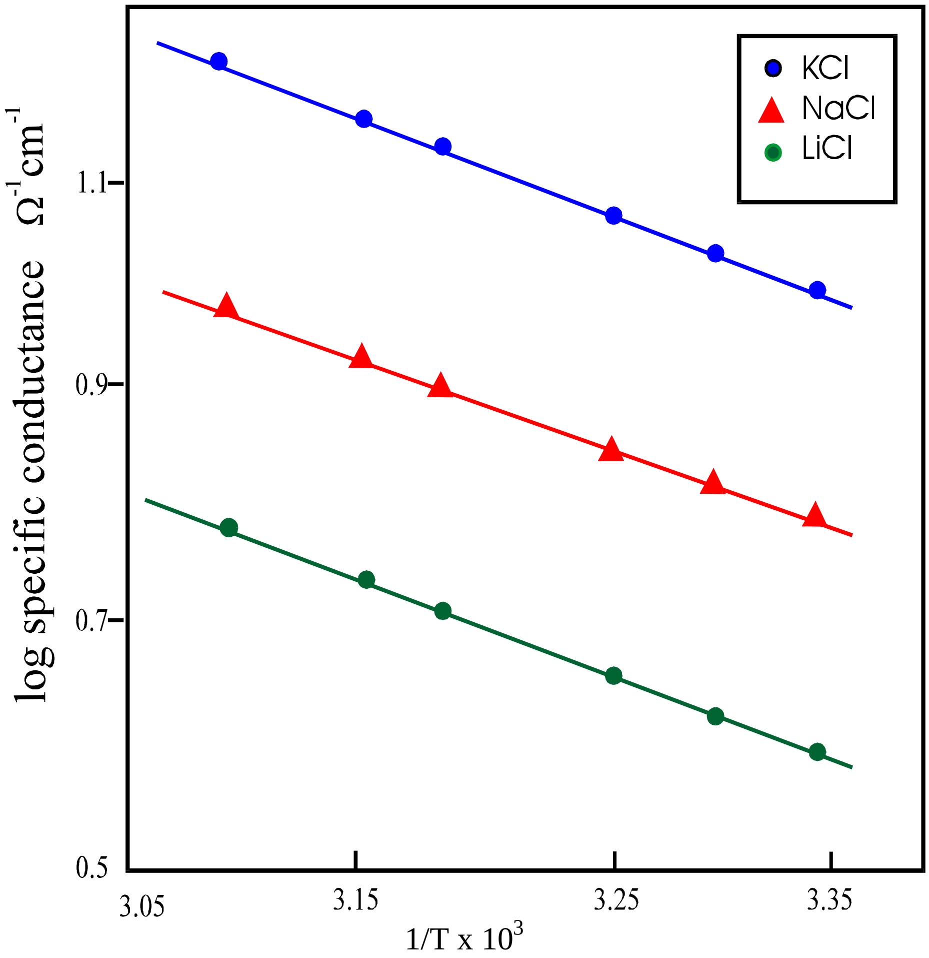

Fig. 7 Arrhenius plot of specific conductance

A reference to Table 7 shows that the activation energy decreases with increase in concentration of the bathing electrolyte solution and that for different electrolytes at a particular concentration it follows the order : $E_{aK}{}^{+} > E_{aNa}{}^{+} > E_{aLi}{}^{+}$, analogous to the sequence of crystallographic radii of the alkali metal cations. When the penetrant moves in a polymer substance containing relatively small amount of water, its motion may be governed by the segmental mobility of the polymer and its diffusivity may depend on the probability that the segment will make a hole large enough to accommodate a penetrant species (21).

In such a system the activation energy will depend on the size of the penetrant species, i.e. the activation energy will increase with the penetrant size. If this is the case in our system, the dependence of the activation energy on the kind of alkali metal ion may be interpreted in terms of the ion's crystallographic radius, which is consistent with the result obtained in the diffusivity measurement in the same system (22).

The thermodynamic parameters, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta F^{\neq}$ have been determined using the theory of absolute reaction rates. Following Eyring (23,24).

$$\pi = \frac{RT}{Nh}\, e^{-\Delta H^{\neq}/RT}\, e^{\Delta S^{\neq}/R} \qquad (1)$$

where π is the membrane conductance, h the Planck constant, R the gas constant, N the Avagadro number and T the absolute temperature. $\Delta F^{\neq}$ is the free energy of activation for the diffusion of ions and is related by Gibbs-Helmoltz equation (2)

$$\Delta F^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (2)$$

ΔH_{+}^{+} is related to Arrhenius energy of activation E_a by the relation (3)

$$E_a = \Delta H^{\neq} + RT \quad (3)$$

A plot of log $\pi Nh/RT$ versus 1/T from experimental data is linear, the slope and the intercept of which give the value for $\Delta H^{\neq}$ and $\Delta S^{\neq}$. This justifies the applicability of Eq. (1) to the system under investigation. The derived values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were then used to get the value of $\Delta F^{\neq}$ and E_a using Eqs (2) and (3). The values of E_a, $\Delta H^{\neq}$, $\Delta F^{\neq}$ and $\Delta S^{\neq}$ for the diffusion of various electrolytes through the membrane are given in Table 7. The results indicate that the electrolyte permeation gives rise to negative values of $\Delta S^{\neq}$. These values may be attributed to the partial immobilization of ions within the membrane most notably due to interstitial permeation and ionic interaction with the membrane fixed charge group.

On the other hand we have (25)

$$\pi = \pi_0 \, e^{-E_a} /^{RT} \quad (4)$$

and

$$\pi_0 = 2.72\left(KTd^2/h\right) e^{\Delta S^{\neq}/R} \quad (5)$$

where K is the Boltzman constant and d is the interionic jump distance, i.e. the distance between equilibrium positions of diffusing species in the membrane. Equation (4) predicts that a plot of log π versus 1/T should be linear from which E_a may be obtained. Substituting the values of $\Delta S^{\neq}$ and E_a in Eqs. (4) and (5) we get the value of interionic distance, $d \approx 1.6\overset{0}{A}$ which is consistent with the empirical values (1-5 $\overset{0}{A}$) used by different investigators.

CONCLUSION

In this work we have prepared polystyrene based nickel phosphate membrane at pressure 4T and measured the conductance through the membrane. The activation energies are found to decrease with the increase in the concentration of the bathing solutions. It is concluded that the membrane is weakly charged. The interionic Jump distance found to be $1.6A^0$.

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