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Conductometric Studies with Polystyrene Calcium Phosphate Membrane

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ABSTRACT: The current study was focussed and stressed on the measurement and estimation of conductivity. The conductivity of the membrane was examined at different temperature ranges (25-50 ± 0.1°C) and electrolyte concentration ranges ($0.01 \le c\ (M) \le 0.5$) using multi-meter respectively. The selectivity of membrane behaviour was inferred on the basis of conductometric studies which had a particular characteristic. Absolute reaction rate theory was applied and conducted to investigate the mechanism of transport of simple metal ions through the specific membrane. The parameters of thermodynamic parameters such as activation energy, enthalpy, entropy, and free energy were calculated using the appropriate method. The membrane resistivity for 1-1 electrolyte solutions was found to decrease in the order such that $Li^+ > Na^+ > K^+$, which is in accordance with an increase in the size of cation. The activation energy increases with an increase in concentration of the electrolyte as it us directly proportional to each other. The membrane was weakly charged and the ionic species retain their hydration shell, at least partially while diffusing through the membrane pores in a gentle manner. All the values of ΔG, ΔH, and ΔS were found to be positive in nature and there is an increases with an increasing temperature in the order likely to be as such $K^+ > Na^+ > Li^+$.

Keywords: Ionic conductivity; alkali halides; composite polystyrene calcium phosphate membrane; Gibbs free energy; membrane conductivity; activation energy

INTRODUCTION

The attention of the scientific researchers is highly engaged in the development of new functional materials for current engineering applications and has been attracted towards hybrid materials commonly based on electrically conductive polymers and inorganic compounds [1&2].These compounds exhibit a specific variety of useful physiochemical properties in addition to chemical stability, possibilities of opening up for their use in energy storage devices [3], electron field emitters [4], chemical sensors [5&6], biological sensors [7&8] and actuators [9] respectively. Considerable interest has been devoted and dedicated in recent years by the research scholars to develop suitable conducting composite materials for the possible application in gas sensors which are widely used. Though research over the past two decades had identified the polymer based conducting composite for gas sensors, there is lot of scope still available and need to be appreciated in developing the alternate composite materials for sensor activity as well. Apart from conjugated polymer applied earlier, composite like carbon composite materials have been used as chemical gas sensors [10&11] in the present era of research.

Phosphate-based molecular sieves [12] have attracted lot of attention in the academics and industry because of their interesting and enthusiastic 2-D and 3-D framework topologies. The cation exchange materials are very common and widely used among inorganic materials (e.g. zeolite), whereas anion exchange inorganic materials are used very rarely in the techniques nowadays [13].The crystalline behaviour and chemical flexibility of PS always ready allow for the more appropriate and handful needs by fabrication in a simple and flexible one-step synthesis, in addition to its cross-linked rigid and stiff framework providing an adequate adhesion to the Ti-As materials. Therefore, it accounts for higher mechanical stability as needed for good results.

The electrical conductivity of the electrolytic solutions is a quite important property having both theoretical and practical significance in everyday life in the experimentation. It highly depends on the nature of the dissolved substances, the solvent in which it get dissolved, the temperature range, and the concentration Models for the inter-ionic interactions that is occurring in solutions of strong electrolytes provide valuable information and enhancing data on ionic behaviour, which is very necessary for the development of new electro-chemical power sources and for understanding the processes and mechanism taking place during the formation of galvanisation , coating or metal refining by the process of electrolysis.

The mathematical foundation used to describe or brief the variation of the equivalent electrical conductance with the solution concentration is quite well developed and enhancing and has been reported in a number of monographs respectively [14&15]. The most widely used equations are those of Fuoss and Onsager [16, 17&18].

The dynamic studies on the electrical conductance of the solutions are related to the investigation of solvation and electro-transport properties of the constituent ions present in the solution. These properties depend on both the characteristic that is the ionic radius as well as the degree of ionic hydration [14-18].

The present investigation is mainly focused on conductivity measurements. In accordance with this study, the analysis of the conductivity of membrane under various conditions required for the electrolyte concentration was carried out in order to understand the mechanism of ionic transport across the membrane surface in a synthesized manner. In addition to resistance, the diffusion coefficient, activation energy, Gibbs free energy, enthalpy and entropy were also investigated randomly.

MATERIAL AND METHODS

2.1. Preparation of membranes:

Polystyrene calcium phosphate membrane was synthesized which was first modified Khan and Rafiuddin method [19]. In brief, pure crystalline polystyrene (Merck Chemicals) was used as a binder, 0.2 M tri-sodium phosphate solution (99.98%, Sigma-Aldrich), 0.2 M calcium chloride (99.98%, Sigma-Aldrich) solution and different electrolyte solutions (KCl, NaCl and LiCl) of various concentrations were also prepared to carry out experimentation.

Calcium phosphate was prepared using specific sol-gel process by mixing 0.2 M aqueous solution of tri-sodium phosphate with 0.2 M calcium chloride solution made by constant stirring of substances at 90 ± 0.2 °C for 2 h. The pH of the mixture was adjusted to 1.0 by randomly adding dilute hydrochloric acid (32%, Merck Chemicals) under constant stirring process and the resultant precipitates were left to age for 24 hours at room temperature (25 ± 0.2 °C) . The obtained precipitate at room temperature was well washed several times with deionised water and dried for 5 h at 100 ± 0.2 °C in a vacuum oven (Binder VD25) for attaining better results.

The composite mixture of the compound polystyrene and calcium phosphate were kept into cast die of diameter 2.45 cm and placed in an oven which was maintained at 200 ± 0.2 ° for about half an hour to equilibrate the reaction mixture and after on the die was transferred to a pressure device (Carver Hydraulic Unit Model 3912, Wabash, USA).

Composite membranes is highly said to be prepared by embedding 25% polystyrene with nickel phosphate and had the highest mechanical stability and reproducible results. Those substances containing greater amounts (> 25%) of polystyrene did not give reproducible results while those with lesser amounts with lesser amounts of polystyrene (< 25%) were found to be unstable [20-22]. The total amount of the mixture utilised for the preparation of the membrane contained 0.063 g of polystyrene and 0.187 g of calcium phosphate respectively.

2.2. Measurement of membrane resistances:

The test cell used for the electrochemical measurements is similar to that described elsewhere [23&24]. Membranes were tightly clamped between two glass half-cells of the membrane conductivity for the precaution as well. The half-cell volume was 50 mL and the effective membrane area was 196.7 mm^2. Various salt solutions such as chlorides of K^+, Na^+, and Li^+ were prepared using deionised water specifically. A magnetic stirrer was placed at the bottom of each half-cell to minimize the concentration-polarization at the membrane surfaces and the measurements of the solutions were carried out at a stirring rate of 500 rpm [25&26]. pH of the solutions were found to be range between 5.5 to 6. The measurements of conductivity in term of resistivity were carried out by adopting one of the qualitative methods followed[23&24] at different temperature (25 ± 50) ± 0.2 °C, which was controlled by an enhancing refrigerated thermostat (Julabo F12-ED).The resistivity through the membrane was recorded which employed a digital multi-meter (T235H, Hellermann Tyton) using two platinum electrodes (RE) from the Radiometer analytical [23&24].For each experimentation three individual measurements of the membrane resistance were taken into consideration and the mean was taken as the desired result..

RESULTS AND DISCUSSION

The diffusion of the specific electrolyte through the membrane is slower than that in the solution. Moreover, the order does not remain the same due to various factors namely: (a) only a small part of the framework is available for free diffusion process; (b) the diffusion paths in the membrane phase are said to be more tortuous; (c) the large hydrated ions in the narrow mesh region of the membrane could be impeded in their mobility; and (d) the interactions of the diffusing species with fixed groups occur on the membrane matrix [27] respectively.

The effective membrane conductivity was determined experimentally as a function of solution concentration maintaining equilibrium with the membrane, which in principle sense can be used for the estimation of membrane resistance. The conductivity σ of the membrane in given by the relation as follows [28]:

$$\sigma = \frac{L}{AR} \tag{1}$$

where L is the thickness of the wet membrane (1.1 mm), A its area (196.7 mm^2) and R its membrane resistance.

The changes in resistance was noted with respect to time is shown in Fig.1 for various 1:1 electrolyte diffusion through membrane enormously. The value of resistance declines slowly with time. At any given time the resistance value for various electrolyte resembles the following order $Li^+ > Na^+ > K^+$, in agreement with other results reported elsewhere [29].

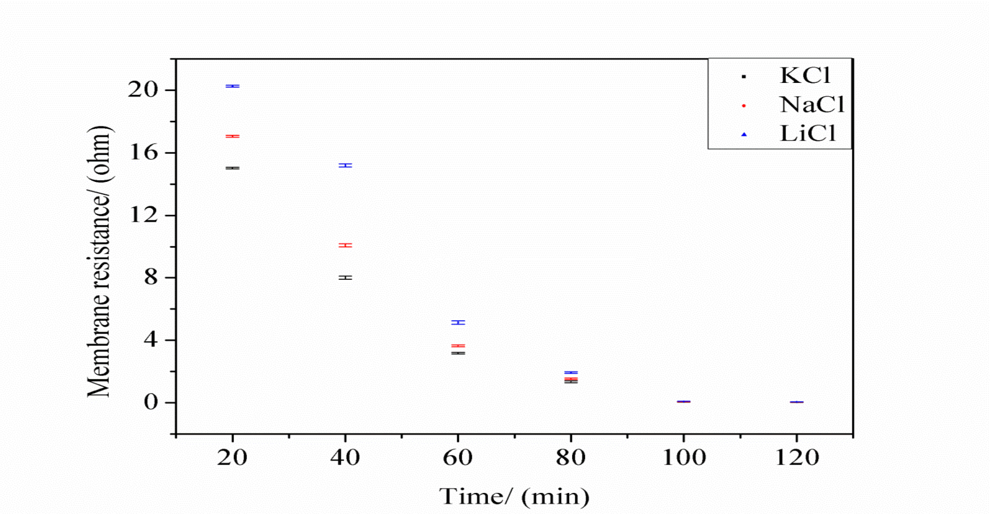

Fig. 1: Plot of membrane resistance *vs*. time for the Polystyrene Calcium Phosphate composite membrane using 0.5 M of 1:1 electrolytes at 25 ± 0.1°C. Each experiment was repeated three times ensuring accuracy of the measurements and the data are shown as mean ± SD's of three individual experiments.

The variation of the conductivity along the membrane with various 1:1 electrolyte concentration at room temperature are shown in Fig.2. The conductivity of the membrane had increased almost non-linearly in the relation of the square root of electrolyte concentration due to the increased obstruction of the polymer matrix as diffusional pathways is found to be more tortuous in concentration solution. It also explaines that at higher concentration the uptake of electrolyte by membrane is higher which results in increased value of conductivity and attains a maximum limiting value at specific range. This is in accordance with the findings and observational reading of Arfin et al.[30] for polyaniline membranes with alkali chlorides. Conductivity of membrane for 1:1 electrolyte solution was found to decrease in the order order $K^+ > Na^+ > Li^+$, which is in accordance with a decrease in the size of the cation respectively as mentioned by *Beg et al.* [31]. This sequence inferred and confirmed that the membrane is weakly charged [32] and the ionic species at least partially retain their hydration shells [33]. The above sequence generally seems to be determined and examined by membrane porosity in relation to size of the hydrated species flowing through it in a considerable way. Although the size of hydrated electrolytes is not known with certainty, there are a few tabulations [14&34] of depicting the number of moles of the water associated with some electrolytes in the solution.

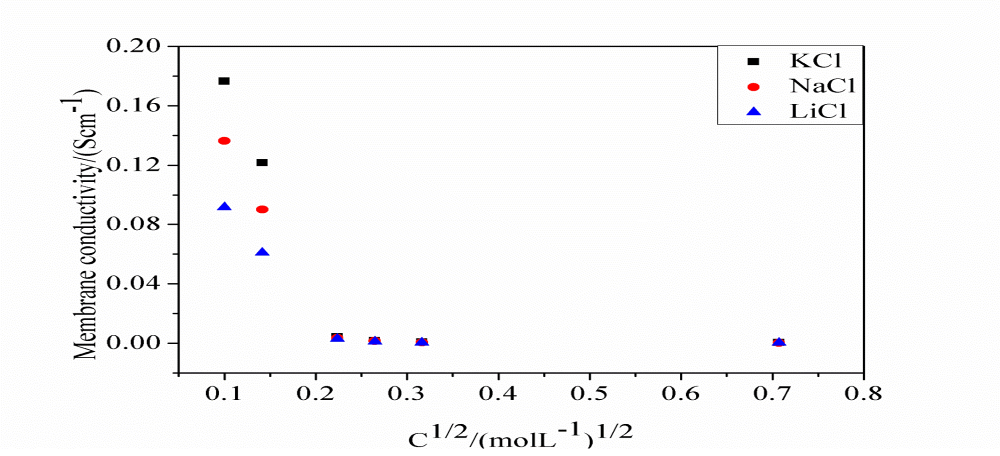

Fig. 2: Plot of membrane conductivity *vs*. concentration for the Polystyrene Calcium Phosphate composite membrane using 1:1 electrolytes at 25 ± 0.1°C.

Ions in the solution are generally solvated when theses ions move in a random way as they carry with them the associated solvent molecules respectively. Ions do not move in stationary medium, but the molecules of the medium travel in the direction opposite to the movement of ions as noted. These counter-currents make it more difficult for the ion to move through the solution and thus slowing down its speed. On dilution both these factors are reduced and speed of ions increases, as a result of which conductivity of the solution also tends to increases. Debye-Hückel and Onsager gave the following relationship between molar ionic conductivity with concentration is given below [14]:

$$\lambda_m = \lambda_m^0 - A\sqrt{c} \tag{2}$$

where A is the constant and it depends on the electrolyte. The above equation represents the equation of a straight line which is not passing through origin $(y = mx + c)$. The extrapolation to a zero concentration gives the limiting equilavent conductivity in Fig.3. The values for molar conductivity of membrane electrolyte systems are given in Table 1. The molar conductivity for a 1:1 electrolyte solution were found to be $K^+ > Na^+ > Li^+$.

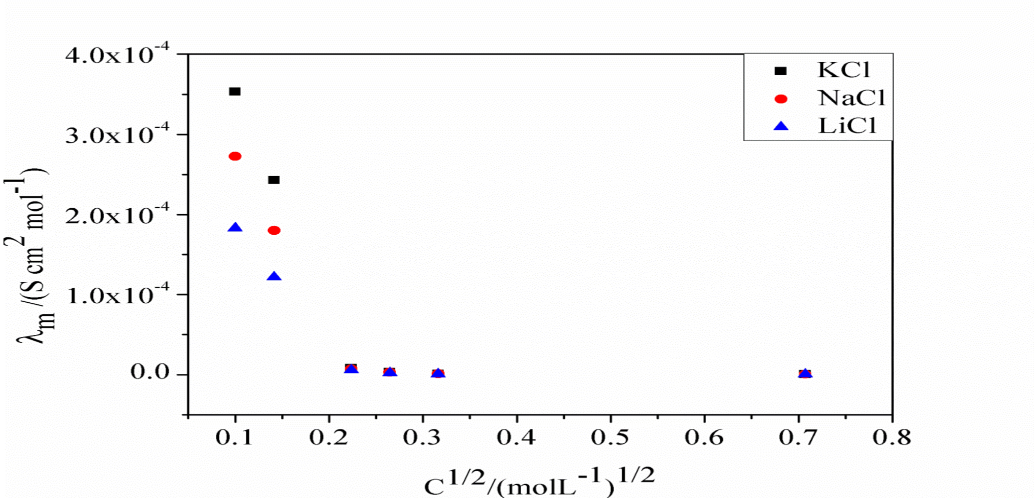

Fig. 3 Plot of membrane molar conductivity *vs*. concentration for the Polystyrene Calcium Phosphate composite membrane using 1:1 electrolytes at 25 ± 0.1°C.

Table 1: Derived values for polystyrene calcium phosphate membrane parameters of λ_m^0 using 1:1 electrolytes at 25 ± 0.1°C.

Electrolytes (mol L^{-1})	λ_m^0 (S cm^2 mol^{-1})
KCl	6.12E-4 ± 8.49E-4
NaCl	4.67E-4 ± 6.47E-4
LiCl	3.14E-4 ± 4.28E-4

The conductivity values was obtained in Fig.4 found to obey the Arrhenius realtion. The Arrhenius equation can be written in a simpler form as [35-37]:

$$\sigma = \frac{\sigma_0}{T}\exp\left(\frac{-E_a}{\kappa T}\right) \tag{3}$$

where σ_0 is the pre-exponential factor of the conductivity, κ is the Boltzmann constant, T is the absolute temperature and E_a is the activation energy for the conductivity.

Taking log the expression gives,

$$\log(\sigma T) = \log \sigma_0 - \left(\frac{E_a}{2.303\kappa T} \right) \qquad (4)$$

The conductivity of membrane for 1:1 electrolyte concentration was found to be strongly dependent on the temperature as an important factor. The conductivity was found to increase exponentially with an increase in temperature. The values of conductivity lie in the order of $10^{-5} - 10^{-3}$ Scm^{-1} i.e., falling under the semi-conductor region [38].

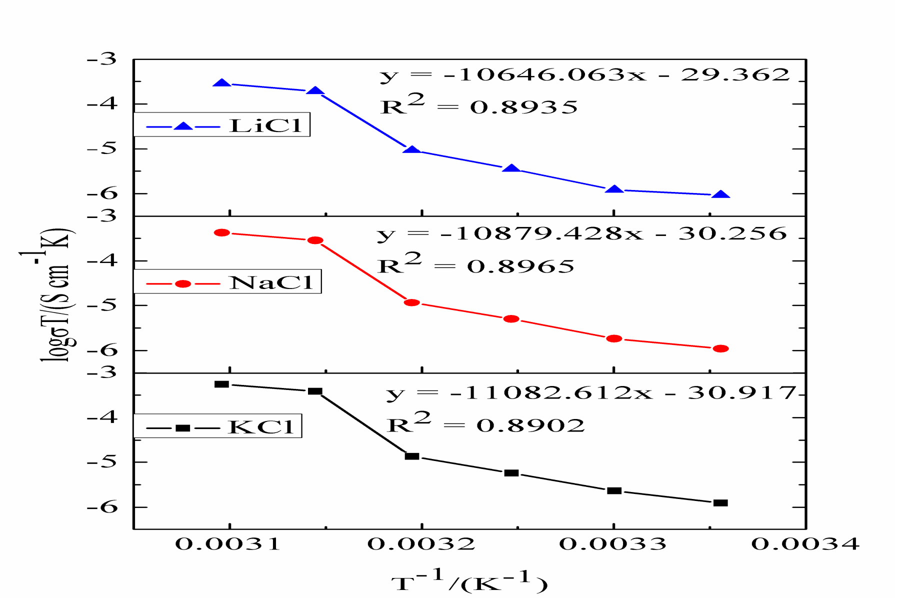

Fig. 4: Plot of membrane conductivity *vs.* temperature for the polystyrene calcium phosphate membrane using 0.5 M of 1:1 electrolytes at (25 - 50) ± 0.1°C

The band energy gap is defined as the difference in energy between the highest point in the valence band and the lowest point in the conduction band. It is representing one of the important optical properties of inorganic semiconductors and can be expressed generally in such a way given follows [39]:

$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-E_g}{2\kappa T} \right) \qquad (5)$$

The factor of $(1/2)$ in the exponent appears with inorganic semiconductors because all the possible distributions of electrons in the conduction band are independent of the distributions of holes in the valence band normally.

From Eqs. (4) and (5), we can get

$$E_a = \frac{E_g}{2} \qquad (6)$$

Hence, the conductivity is thermally activated with activation energy which is equal to half the band gap.

The activation energy (eV) for 1:1 electrolyte solution was calculated from the slope of Arrhenius plots by using linear regression method in accordance with the equation given above and is tabulated in Table 2. It was observed that the activation energy is closely related to the electronegativity of the metal ions and dependent on each other. With a decrease of the electronegativity of metal ion, the activation energy is also found to be increased.

Table 2: Activation energies and band gap energies of conduction for the polystyrene phosphate membrane using 0.5 M of 1:1 electrolytes at (25 - 50) ± 0.1°C

Electrolyte (mol L^{-1})	Activation energy (eV)	Band energy gap (eV)
KCl	2.199	4.398
NaCl	2.158	4.316
LiCl	2.112	4.224

The variation of the activation energy along with the membrane and various 1:1 electrolyte concentration at room temperature are shown in Fig.5. It shows that the activation energy depends on the electrolyte concentration increases with an increasing concentration due to the nature of the sovent and for that different electrolytes at a particular concentration, if follows the order generally $K^+ > Na^+ > Li^+$ are analogous to the sequence of crysrallographic radii of the alkali metal cations. When the penetrating species moves in a polymer substance which is significantly containing relatively small amount of water, its motion can be governed by the segmental mobility of the polymer and its diffusiveness can depend on the probability that the segment would make a hole large enough to accommodate a penetrate species in its specific surrounding[40].

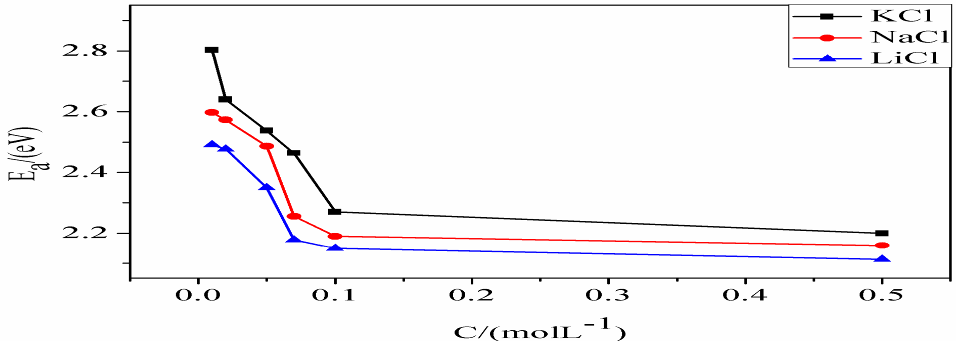

Fig. 5: Plot of activation energy *vs*. concentration for the polystyrene calcium phosphate membrane using 1:1 electrolytes at 25 ± 0.1°C.

One of the quantitative as well as qualitative methods for describing the temperature dependence of the membrane conductivity is the kinetic methods, which uses the results widely from Eyring theory [34&41]. Based on this theory, the thermodynamic characteristics of ion migration can be calculated, for example: the changes of Gibbs energy ΔG, entropy ΔS and enthalpy ΔH for the formation of the activated complex of reacting substances in standard state are represented below as [42]:

$$k = \frac{\chi \kappa T}{h} \exp\left(\frac{-\Delta G}{RT}\right) \tag{7}$$

where k is the rate constant of the process, χ is the transmission coefficient, h is the Planck's constant, and the other parameters are as usual as mentioned above.

According to the two basic theories that is, kinetic theory of ionic conductivity and the theory of the absolute reaction rates, the ions migrate in an electrolytic solutions through a series of jumps, each of them associated with length L and certain change of the partial mole energy of activation ΔG. For this reason, the conductivity σ is directly connected to the properties of both ion and the solvent which can be regarded as a rate constant of the ion translation which that generally occurs as a result of quantum transitions from one stable equilibrium state to another state respectively. From this point of view, the transmission coefficient χ accounts for the possibility to follow the principal for translation of the ion along the three axes of the possibility for translation of the directions. Thus, it is assumed to be equal to $1/6$ and accordingly the equation of Eyring can be written as:

$$\sigma = \frac{|z_\pm| e_0 F}{6h} L^2 \exp\left(\frac{-\Delta G}{RT}\right) \tag{8}$$

Where $|z_\pm|$ is the ion charge, e_0 is the elementary charge, F is the Faraday constant, L is the average distance of ionic jump from one quasi-equilibrium states to another.

Taking into account the relationship between the basic thermodynamic functions and properties, the equation is shown below [14]:

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

Then eqn. (8) can be rewritten in the form [34]:

$$\sigma = \frac{|z_\pm| e_0 F}{6h} L^2 \exp\left(\frac{-\Delta S}{R}\right) \exp\left(\frac{-\Delta H}{RT}\right) \tag{10}$$

There is no other independent method for measuring the length of the activated jump L, that is why it is usually assumed to be equal to the edge of a cube corresponding to the solvent molecule volume:

$$L = \left(\frac{V_m}{N}\right)^{1/3} \tag{11}$$

where V_m is the molar volume of the solvent and N is Avogadro number. The molar volume of the solvent can be calculated from the ratio [43]:

$$V_m = \frac{M}{d} \tag{12}$$

where M is the molar weight and d is the solvent density at a given temperature. After some transformations in the equation and taking the logarithm of Eq. (8) the following equation was obtained [43]:

$$\Delta G = RT\left[\ln \frac{|z_\pm| e_0 F}{6h(N)^{2/3}} + \frac{2\ln V_m}{3} - \ln\sigma\right] \tag{13}$$

With this equation, ΔG can be calculated at any temperature, provided the values of V_m and σ are known for this temperature as well.

If the dependence of ΔG on a particular temperature is known, and the coefficients in the empirical equation for this dependence are known, then the value of ΔS can be calculated by differentiating this equation with respect to temperature in a very synthesized manner [43]:

$$\Delta S = \frac{-dG}{dT} \tag{14}$$

Using the values of ΔS obtained at different temperatures, the values of ΔH can be calculated by the well known relation of thermodynamics as mentioned in Eq. (9). By applying Eq. (13), the temperature dependence of the change of the Gibbs free energy for ionic migration was calculated systematically.

Fig. 6 shows that among the three curves presented only the K^+ has a maximum value. The value of ΔG increases with an increase in the concentration and follows the trend such as $K^+ > Na^+ > Li^+$.

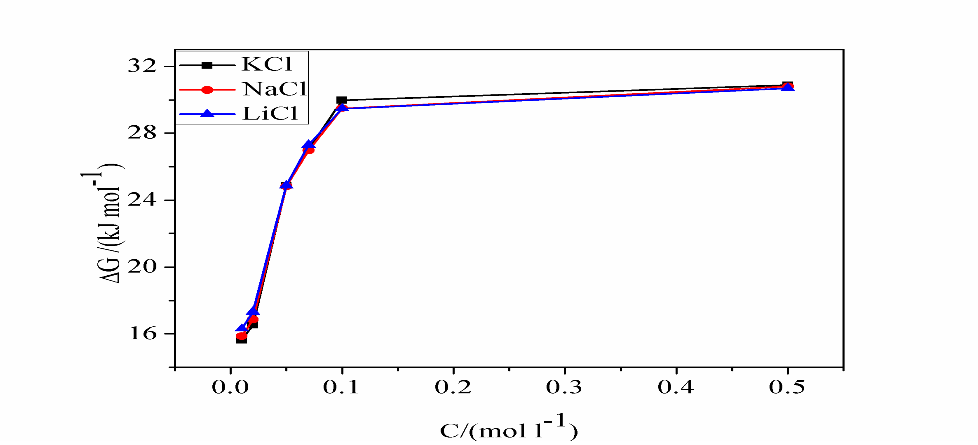

Fig. 6: Plot of Gibbs energy *vs*. concentration for the polystyrene calcium phosphate membrane using 1:1 electrolytes at 25 ± 0.1°C.

Fig.7 shows that the values of ΔG are positive in all the cases depicted above, where the process of ion migration is energetically disturbed since the ion should surmount at certain energetic barrier in a specific behaviour. Irrespective of the nature of solvent, the values of ΔG for K^+ ions are higher than those of Na^+ ions, because they have greater mass, radius and hydration number which is generally of much important. Fig.7 also show that slight decrease in the value of ΔG with the certain increase of temperature is due to the two diversified factor that is: enhanced translation of solvent molecules and the disturbance of its quasi-crystalline structure which generates the necessary "vacancies" for the motion of the ions and decrease in the number of molecules in its hydration shell it is facilitated generally [43]. Thus, ΔG values for an electrolytes follow the sequence for representing the cations in the order such as $K^+ > Na^+ > Li^+$.

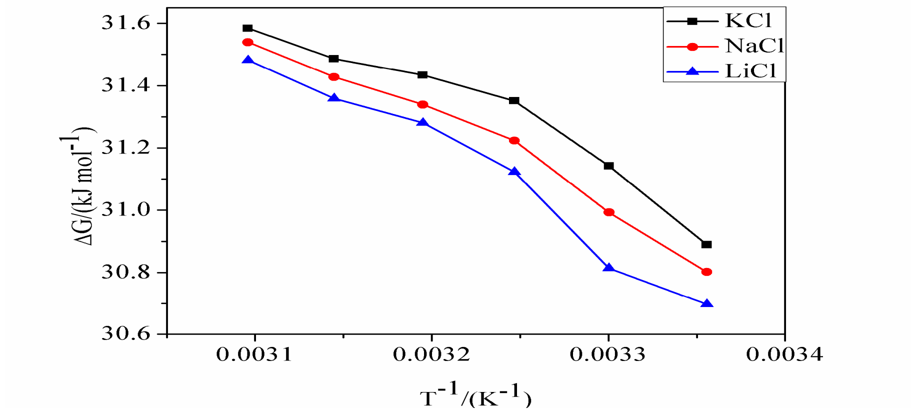

Fig. 7: Plot of Gibbs energy *vs*. temperature for the polystyrene calcium phosphate membrane using 0.5 M of 1:1 electrolytes at (25 - 50) ± 0.1°C

Fig.8 shows that the values of ΔS increase with the increasing electrolyte concentrations in a gentle manner and follows the trend such as $K^+ > Na^+ > Li^+$ which is due to the concentration dependence of the electrolyte. The values hardly differ even though the different electrolyte was employed.

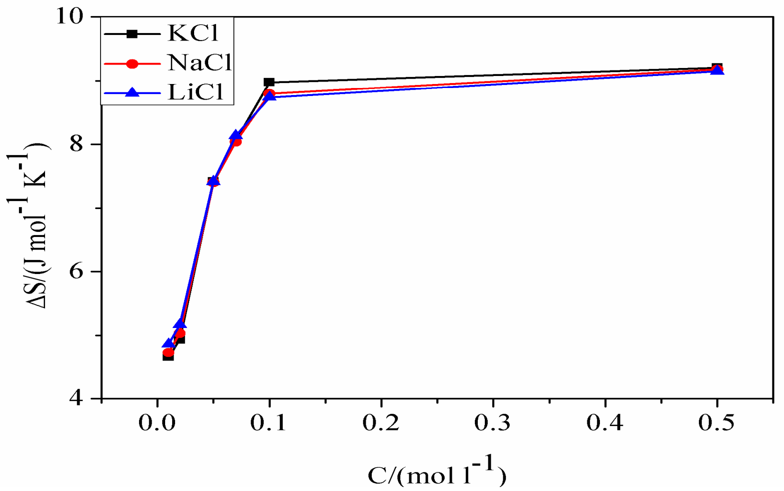

Fig. 8: Plot of entropy *vs*. concentration for the polystyrene calcium phosphate membrane using 1:1 electrolytes at 25 ± 0.1°C.

Fig. 9 shows that ΔS is positive for all cases and corresponds to other. Independent of the nature of the solvent, the values of ΔS for K^+ ions are higher than those for Na^+ ions, because K^+ ion has greater number of molecules in its hydrated shell than the Na^+ ions. The values of ΔS significantly decreases with the increase of temperature, firstly due to the disturbance of the solvent structure and secondly with an improved arrangement of the molecules in the ion hydration shell [44].Therefore, ΔS for 1-1 electrolytes were found to increase in the order generally $K^+ > Na^+ > Li^+$.

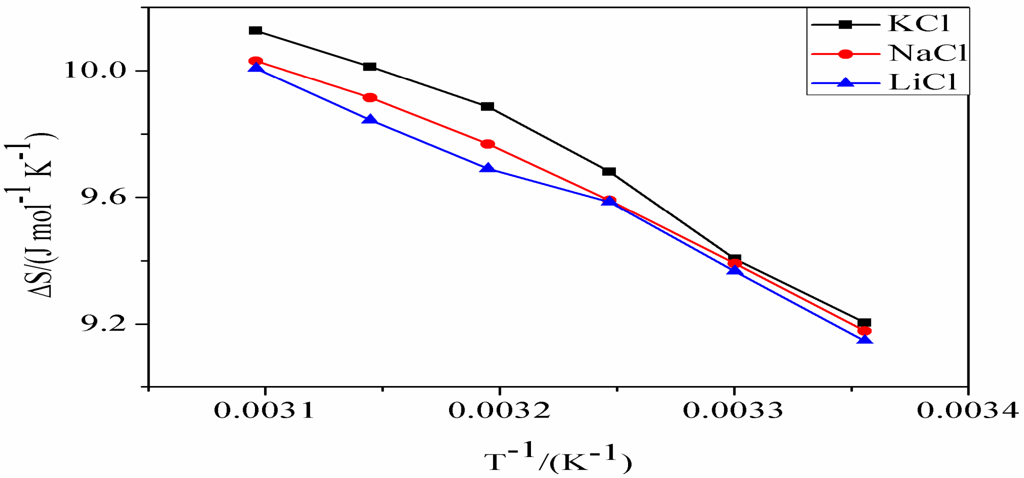

Fig. 9: Plot of entropy *vs*. temperature for the polystyrene calcium phosphate membrane using 0.5 M of 1:1 electrolytes at (25 - 50) ± 0.1°C

Fig.10 shows that ΔH increases rapidly with an increase in electrolyte concentration in the order $K^+ > Na^+ > Li^+$ and this is attributed to the concentration dependence of the electrolyte filling the membrane matrix.

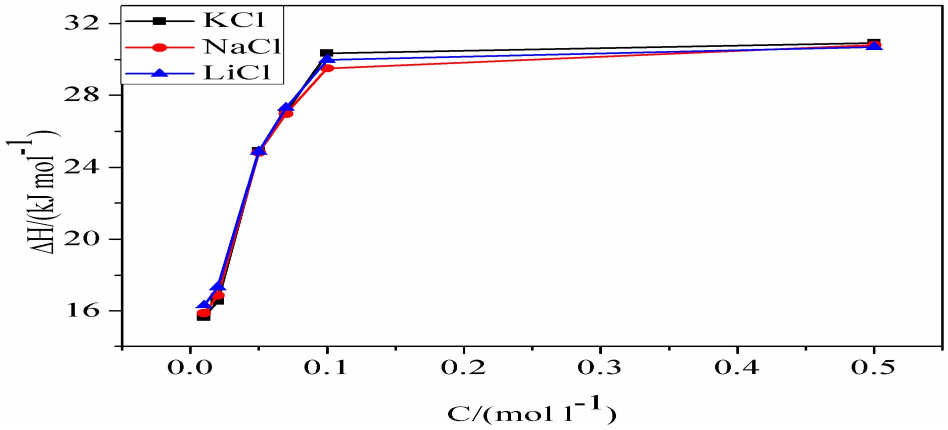

Fig. 10: Plot of enthalpy *vs*. concentration for the polystyrene calcium phosphate membrane using 1:1 electrolytes at 25 ± 0.1°C.

The values of ΔH were calculated and estimated for the three ions at different temperature and the resulting values are presented in Fig. 11. The positive values of ΔH for all the three ions shows their translation to occur in the solution, where a certain amount of energy needs to be introduced in order to overcome the energetic barrier for the migration of water molecules present in the ionic hydration sphere respectively. It can be seen and observed from Fig.11 that the values of ΔH decrease with an increase of temperature and it states that it is inversely related to each other. The different slopes of the straight lines formed can be explained by the different strength of hydration of water that are bound to the ions of the membrane, it can be stated that the transition of the ions within the solution from one equilibrium state to another is easier when the bonding of the hydration sphere to the ion is weaker and a smaller number of water molecules is transported and directed with the ion during translation process.

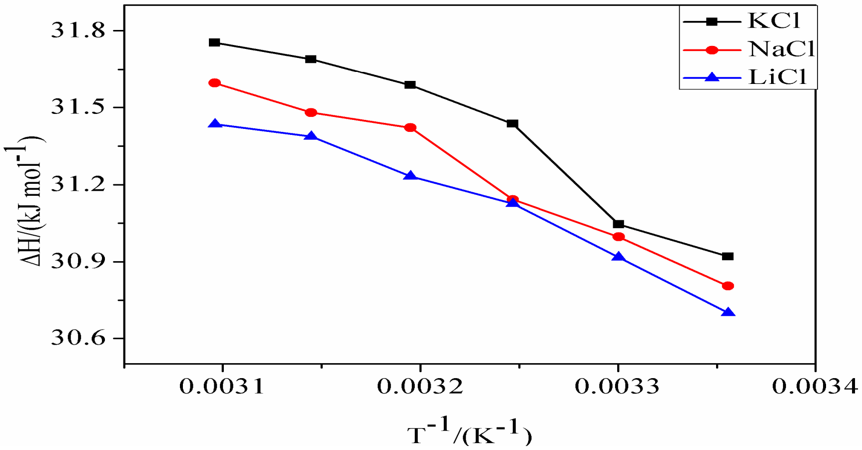

Fig. 11: Plot of enthalpy *vs*. temperature for the polystyrene calcium phosphate membrane using 0.5 M of 1:1 electrolytes at (25 - 50) ± 0.1°C

Fig. 12 shows that a system with a higher entropy change ΔS will require less activation energy for its thermal dehydration. Such dependence was also observed for the thermal decomposition of other compounds in an adequate behaviour [45].

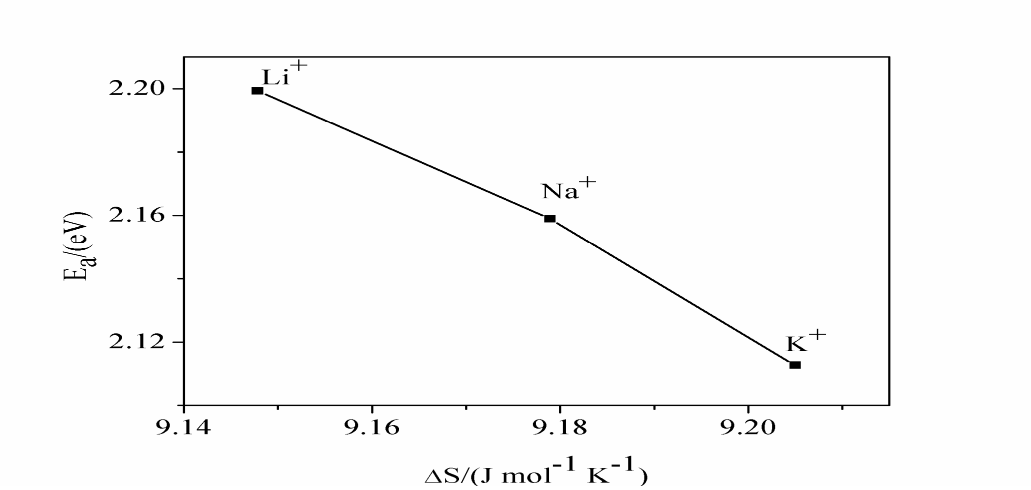

Fig. 12: Plot of activation energy *vs*. entropy for the polystyrene calcium phosphate membrane using 0.5 M of 1:1 electrolytes at 25 ± 0.1°C.

CONCLUSION

In this communication, the resistivity measurement data across polystyrene calcium phosphate membranes were used by applying the various methods based on thermodynamics of irreversible processes. At the same time it was experimentally observed that the membrane conductivity were used to compute various thermodynamic parameters namely, activation energy, entropy, enthalpy and free energy by the application the theory of absolute reaction rate. The results of all these investigations and sequencing are that membrane conductivity can be determined at different temperatures ranges with reasonable accuracy in an experiment. As a result it was inferred that "the membrane is weakly charged and ionic species retain their hydration shell at least partially while diffusing through the membrane pores."

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