

*Full Paper*

## **Ionic Conductivity of Alkali Halides across a Polyaniline-Zirconium (IV)-Arsenate Membrane**

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*Received: 2 February 2013 / Accepted: 10 April 2013 / Published online: 30 April 2013*

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**Abstract-** In continuation to our previous work with composite polyaniline-zirconium (IV)-arsenate (PZA), we further extended with the conductivity measurements in this report. All the calculations reported in here were extracted from the experiments carried out in the temperature range of (25-50)±0.1°C and at different concentrations (0.01≤C(M)≤1) of KCl, NaCl and LiCl 1-1 electrolyte solutions. The diffusion coefficient for 1-1 electrolyte solutions was found to decrease in the order K<sup>+</sup>> Na<sup>+</sup>> Li<sup>+</sup>, which is in accordance with a decrease in the size of cation. The resistance is decreasing with increasing time in the order Li<sup>+</sup>> Na<sup>+</sup>> K<sup>+</sup>, and is due to an increased size of the cation for the chosen electrolytes. From the results, the conductivity values for 1-1 electrolytes in the membrane phase were found to be higher at the lower concentration for all the electrolytes in the order of Li<sup>+</sup>> Na<sup>+</sup>> K<sup>+</sup>. It was observed that the conductivity found to be increased with an increase of temperature and obeyed the Arrhenius equation. The activation energy increased with an increased concentration of electrolyte solution and the sequence for the energy of activation is Li<sup>+</sup>> Na<sup>+</sup>> K<sup>+</sup>. The Gibbs free energy, enthalpy and entropy for the ions were calculated at different concentrations and temperatures. All the values of ΔG, ΔH, and ΔS were found to be positive in nature and are following the order K<sup>+</sup>> Na<sup>+</sup>> Li<sup>+</sup>.

**Keywords-** Ionic Conductivity, Alkali Halides, Composite Polyaniline Zirconium (IV) Arsenate Membrane, Gibbs Free Energy, Membrane Conductivity, Diffusion Coefficient, Activation Energy

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## 1. INTRODUCTION

In the last few decades, the organic-inorganic ion exchange materials have been extensively investigated for academic and industrial purpose. These materials are formed by developing organic polymers and inorganic particles are important for the environmental applications. The organic ion exchangers have an extensive applicability but few limitations such as poor thermal stability, i.e., very unstable at high temperature and strong radiation. However, the inorganic ion exchangers have their own limitations such as non-suitable for column operation due to granulometric nature. In order to overcome the limitations of organic and inorganic ion exchangers, many investigators introduced the improved materials by the incorporation of organic monomers into inorganic matrix. These composite materials are attractive with a better chemical, thermal and mechanical stabilities, reproducibility, functionality, hydrophobicity, electrochemical and optical as well as magnetic properties [1,2].

Polyaniline exists in a various forms that differ in chemical and physical properties [3,4]. It is an electrically conducting polymer and due to its unique electrical, electrochemical, and optical properties, has been used as a rigid material and is fragile, insoluble even in organic solvents [5]. It has recently achieved extensive importance because of its unique conduction mechanism and high environmental stability. It has good affinity for ion-exchange membranes and also polymerizes in the membrane matrix by chemical oxidation. However, zirconium arsenate is a crystalline with triclinic space group  $P\bar{1}$  in nature. The Zr atoms display normal octahedral geometries with As-O bond distances close to the expected values [6], and possess excellent ion-exchange capacity.

An ion-exchange membrane is considered as a micro-heterogeneous system. According to the model proposed by Gnusin *et al.* [7], Zabolotsky and Nikonenko [8], the ion-exchange membrane is considered as a combination of a 'gel phase' with a relative uniform distribution of functional groups and a hydrophilic part of the polymer matrix chains impregnated with a charged solution compensating the charge of the fixed groups. It was also shown [9] that the micro-heterogeneous structure of the membrane material is the main factor for determining the concentration dependence of the membrane transport properties such as the electrical conductivity, diffusion permeability, and transport numbers. It is a well-known fact that the alkali halides inherit better conductivity values than any other electrolytes. An alkali halide consists of a salt dissolved in a solvent, and their conductivity values therefore depend on the salt concentration as well as the solvent concentration.

We previously reported [10] the synthesis, characterization, ion-exchange behaviour and analytical applications of polyaniline-zirconium (IV)-arsenate (PZA) composite material; however, the present investigation is focused on the extension of our studies further with conductivity measurements. In this study, the analysis of the conductivity of membrane under various conditions of the electrolyte concentration was carried out in order to understand the

mechanism of ionic transport across the membrane surface. In addition to resistance, the diffusion coefficient, activation energy, Gibbs free energy, enthalpy and entropy were also investigated.

## 2. EXPERIMENTAL

### 2.1. Reagents

The main reagents used for synthesizing polyaniline zirconium (IV) arsenate were obtained from LobaCheme (India Ltd., used as received). All other reagents and chemicals were of analytical grade and used without further purification.

### 2.2. Preparation of membranes

During the synthesis of the PZA composite membrane, we first prepared zirconium (IV) arsenate by mixing 0.2 M zirconium (IV) oxychloride with 0.2 M sodium arsenate. The pH of the mixture was adjusted to 1.0 by adding 1 M HNO<sub>3</sub> under constant stirring and the resultant white precipitates were left to age for 24 h at room temperature.

Following this, the PZA membrane was prepared by the procedure as described by Nabi *et al* [10]. Accordingly, the zirconium (IV) arsenate precipitate was mixed with 10% polyaniline under constant stirring and the resultant precipitates were left to age for 24 h at room temperature. The precipitate was washed with ultra-pure distilled water several times and was made to dry at 50±0.2 °C. The dried products were converted to the H<sup>+</sup> form via the addition of 1 M HNO<sub>3</sub> solution and washed with ultra-pure distilled water several times and finally dried at 50±0.2 °C. All the membranes were prepared by pressing the powder of the composite into pellets employing a hydraulic press (Carver Hydraulic Unit Model 3912, Wabash, USA).

### 2.3. Measurement of membrane resistances

The test cell used for the electrochemical measurements is similar to that described elsewhere [11,12]. Membranes were tightly clamped between two glass half-cells for the electrochemical measurement of the membrane conductivity. The half-cell volume was 50 ml and the effective membrane area was 196.7 mm<sup>2</sup>. Various chloride salt solutions of group 1 elements, namely, K, Na, and Li, were prepared with ultrapure water produced by a Milli-Q Gradient unit (Millipore) and the half-cell filled with these electrolyte solutions. A magnetic stirrer was placed at the bottom of each half-cell to minimize concentration-polarization at the membrane surface and measurements were carried out at a stirring rate of 500 rpm [13-15]. The pH values of the prepared solutions were found to be between 5.5 and 6. Membrane conductivity in terms of membrane resistance was measured at different temperature (25-50)±0.1°C, which was controlled by a refrigerated thermostat (Julabo F12-ED). The conductivity through the membrane was recorded employing a digital multimeter

(T235H, Hellermann Tyton) using two platinum electrodes (RE) from Radiometer analytical [16]. On each system three individual measurements of the membrane resistance were made and the mean was taken as the desired result.

#### 2.4. Cation diffusion coefficients through membrane

Diffusion of ions was determined by measuring conductivity of both containers with respect to time. The geometric characteristics of the cell can be grouped into a constant  $\beta$ , may be called as cell constant, and estimated by [17].

$$\beta = \frac{A}{L} \left( \frac{1}{V_1} + \frac{1}{V_2} \right) \quad (1)$$

Where  $A$  is effective membrane area (196.7 mm<sup>2</sup>),  $L$  the membrane thickness (1.1 mm),  $V_1$  and  $V_2$  are the volume of solutions used in containers 1 and 2 (50 ml).

From Fick's second law for diffusion can be written as:

$$\frac{\partial C^2}{C^1 - C^2} = \beta D \partial t \quad (2)$$

Under the conditions,  $t=0$  to  $t=f$ , integrated the eqn. (2) is,

$$\int_0^f \frac{\partial C^2}{C^1 - C^2} = \beta D \int \partial t \quad (3)$$

Finally get the equation as:

$$\ln \left( \frac{C_f^1 - C_f^2}{C_0^1 - C_0^2} \right) = -\beta D t \quad (4)$$

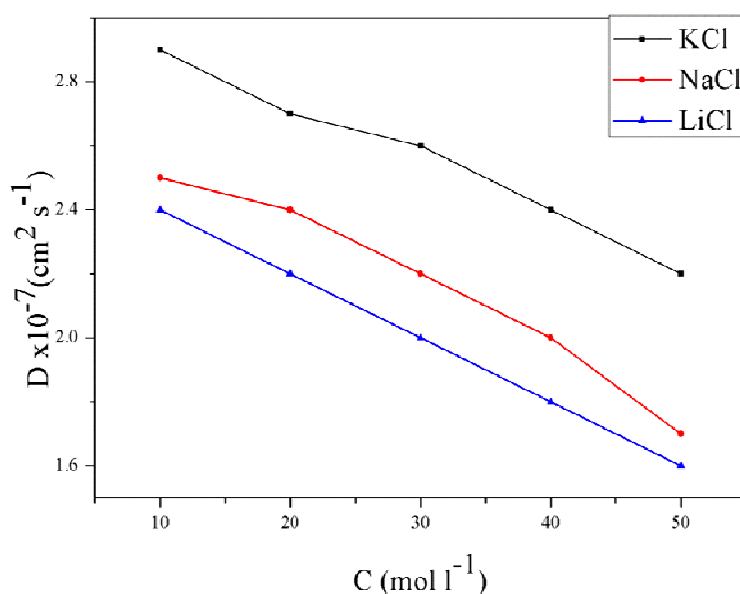
Where  $C$  is the final concentration or initial concentration in the container 1 or 2,  $D$  the diffusion coefficient,  $t$  the diffusion time. The super and subscripts are  $0$ , initial;  $f$ , final; 1, container 1; 2, container 2. By eqn. (1), diffusion coefficients of different cations ( $K^+$ ,  $Na^+$  and  $Li^+$ ) were determined. 0.01-0.1 M initial electrolyte concentrations were taken.

### 3. RESULTS AND DISCUSSION

In our previous work [10], we reported the synthesis of PZA composite and a depth characterization by Scanning Electron Microscopy (SEM), Thermal Gravimetric Analysis-Derivative thermogravimetric analysis (TGA-DTG), Fourier Transform Infrared

Spectroscopy (FTIR), X-ray Diffraction (XRD), chemical stability, thermal stability, *etc.* In this study, we carried out the conductivity measurements under various conditions.

The dependence of diffusion coefficient values to electrolyte concentration for the membrane is shown in Fig. 1. In all cases, a decrease of diffusion coefficient with increasing electrolyte concentration was found and this is attributed to the concentration dependence of the electrolyte filling the membrane matrix. The diffusion coefficient values for the electrolytes follow the sequence for the cations in the order  $K^+ > Na^+ > Li^+$ , which is in accordance with a decrease in the size of the cation [18].



**Fig. 1.** Plot of membrane diffusion rate vs. concentration for the PZA composite membrane using 0.01-0.1 M of 1:1 electrolyte at  $25 \pm 0.1$  °C. Each experiment was repeated three times ensuring accuracy of the measurements and the data are shown as mean of three individual experiments

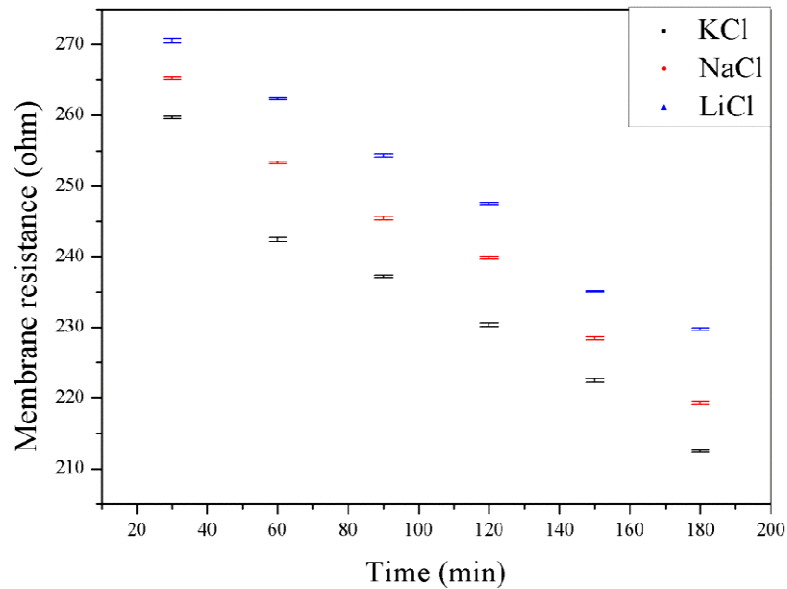
The diffusion of electrolytes is found to be slower than in the free solution as well as the order does not remain the same is due to various factors, such as (a) only a part of the frame work is available for free diffusion (b) the diffusion paths in the membrane phase are more tortuous and therefore longer (i.e. tortuosity factor) (c) the larger hydrated ions in the narrow mesh region of the membrane might be impeded in their mobility by the frame work and (d) the interaction of the diffusing species with the fixed groups on the membrane matrix.

The conductivity  $\sigma$  of the membrane is given by the relation:

$$\sigma = \frac{L}{AR} \quad (5)$$

where R is the membrane resistance.

The time dependence of resistance of the membrane for 1:1 electrolytes is shown in Fig. 2. From the Fig. 2, it appears that resistance decreases with increasing time and follows the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ , in agreement with other results reported elsewhere [18].



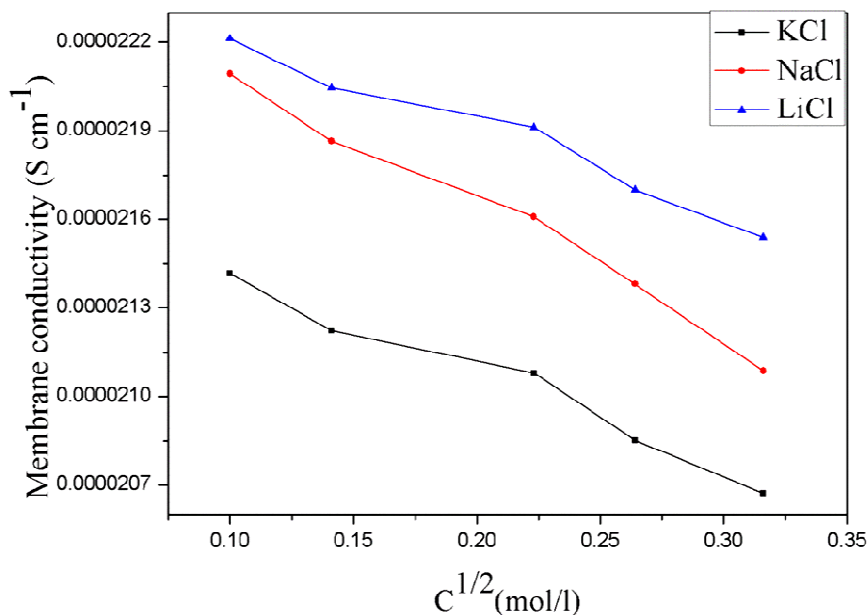
**Fig. 2.** Plot of membrane resistance vs. time for the PZA composite membrane using 0.1 M of 1:1 electrolytes at  $25 \pm 0.1$  °C. Each experiment was repeated three times ensuring accuracy of the measurements and the data are shown as  $\text{mean} \pm \text{SD}$ 's of three individual experiments

The membrane conductivity variation for 1:1 electrolytes at room temperature with different electrolyte concentrations is shown in Fig. 3. The room temperature membrane conductivities are comparable with the values reported in literature for similar compositions [19,20]. The variation follows the trend; as electrolyte concentration increases, conductivity decreases and then reaches to the maximum.

The temperature range from 25 to 50 °C, the membrane conductivity ( $\sigma$ ) measured in this way obeyed the Arrhenius equation:

$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

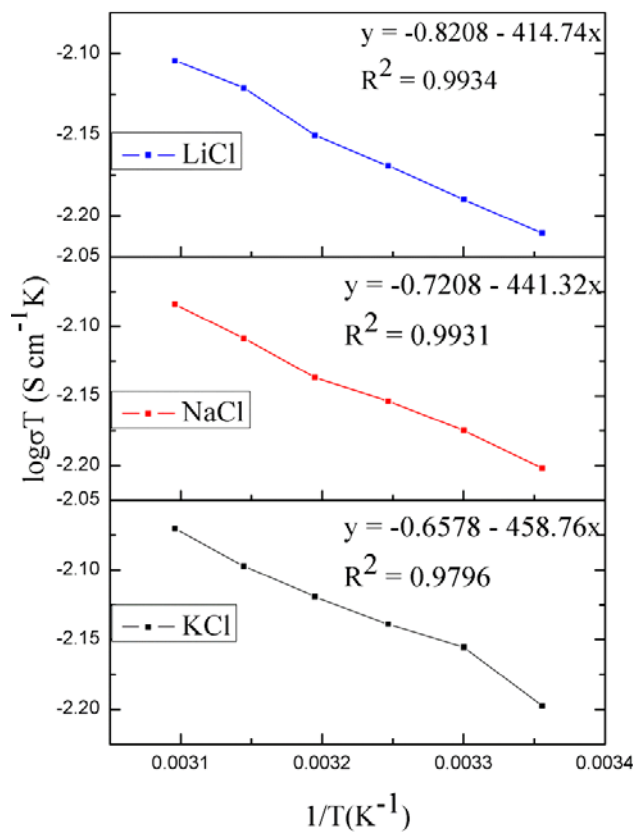
Where  $\sigma_0$  is the pre-exponential factor of the conductivity,  $\sigma_0$  actually depends on temperature, but less rapidly than exponentially, R the gas constant, T the absolute temperature in K and  $E_a$  the activation energy for the thermally activated process.



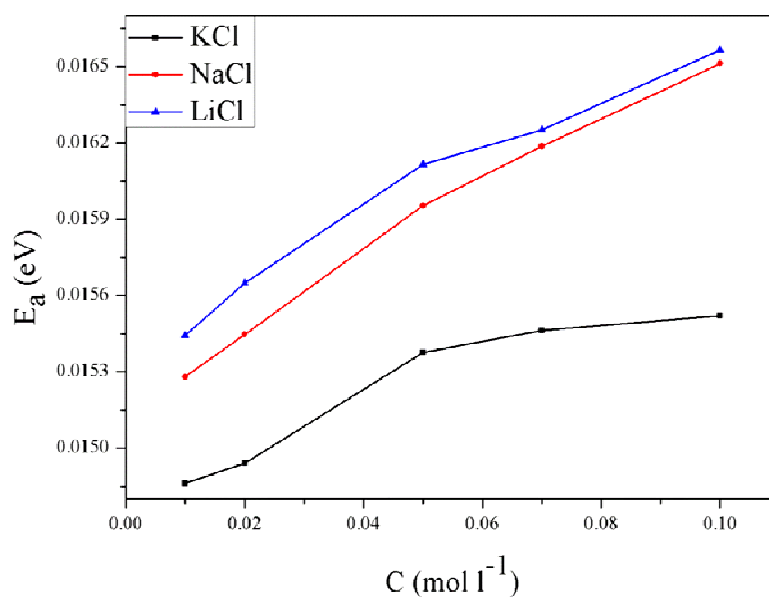
**Fig. 3.** Plot of membrane conductivity vs. concentration for the PZA composite membrane using 0.1 M of 1:1 electrolytes at  $25\pm 0.1\ ^\circ C$

The temperature-dependence of the membrane conductivity for 1:1 electrolytes is shown in Fig. 4. From the Fig. 4, it appears that the conductivity increases with increasing temperature [19-22]. The activation energies (eV) in Fig. 4 were calculated from eqn. (6) using least squares analyses of the experimental data. These activation energies followed the opposite trend of membrane conductivity i.e. as the conductivity increases the activation energy decreases.

This study also extends the scope of the Arrhenius equation to electrolyte concentrations. Fig. 5 shows that the activation energy depends on the electrolyte concentration and increase with increasing concentration [23]. From Fig. 5 demonstrate that even though electrolyte concentration and electrolyte type do affect the energy of activation, the dominant factor affecting the activation energy appears to be the nature of the solvent. Fig. 5 clearly shows that the values of the activation energy increased with an increase in the size of cation. It means that the thermal stability of the crystallohydrates studied increased regularly with the increase in a size of the cation.



**Fig. 4.** Plot of membrane conductivity vs. temperature for the PZA composite membrane using 0.1 M of 1:1 electrolytes at  $(25-50) \pm 0.1 \text{ }^\circ\text{C}$



**Fig. 5.** Plot of activation energy vs. concentration for the PZA composite membrane using 1:1 electrolytes at  $25 \pm 0.1 \text{ }^\circ\text{C}$

It is well known that the basic equation of Eyring from the theory of activated complex (transition state) for reactions may be written in the following form [24]:

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

Where  $k$  is the reaction rate constant,  $\chi$  the transmission coefficient,  $k_B$  the Boltzmann constant,  $h$  the Planck constant,  $\Delta G$  the change of Gibbs free energy for the formation of the activated complex by the reagent, and  $R$  and  $T$  have their usual meaning. According to the kinetic theory of ionic conductance and the theory of the absolute rates of reactions [25], ions in aqueous solutions of electrolytes migrate as a result of quantum transitions from one stable (equilibrium) state to another. In addition, each elementary transition occurs at distance  $l$  and is accompanied by certain change of the partial molar free energy of activation for this process,  $\Delta G$ . for this reason, the conductance,  $\sigma$ , has a characteristic value directly connected with the properties of ions in the solution. By this approach, the translation coefficient  $\chi$  accounts for the possibility of a given ion moving forward or backward along the three coordinate axis. Therefore, its value is  $\chi=1/6$ , and using the equation of Eyring for ionic-conductance yields the following form [26]:

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

Where  $z$  is the ion valency,  $e_0$  is electron charge,  $F$  is Faraday's constant,  $L$  is the average distance of ionic jump between two quasi-equilibrium states, and  $\Delta G$  is change of the isobaric potential per mole of ions from this "jump". The last two parameters can be interpreted as kinetic parameters of the process of ionic-conductance. It should be noted that all changes in the system of a dissolved substance plus the solvent affect the values of  $L$  and  $\Delta G$  due to changes in the solvent structure. Furthermore, the absolute value of these changes should be maximal at infinite dilution of the solutions. That is,  $\sigma$  is an exponential function of  $\Delta G$ . Therefore, eqn.(8) is usually used to calculate the kinetic parameters of the ions, taking into accounts the temperature dependence of the conductances of ions [26].

Taking into account the relation between the basic thermodynamic functions [27]:

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

Then eqn. (8) can be rewritten in the form [28]:

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

Where  $\Delta S$  is the entropy and  $\Delta H$  is the enthalpy of the system. There is no independent method for determining the length of the activated jump  $L$ , it is most often assumed that its values are equal to the length of the edge of a cube corresponding to the volume of a solvent molecule [29]:

$$L = \left( \frac{V_m}{N_A} \right)^{\frac{1}{3}} \quad (11)$$

Where  $V_m$  is the molar volume of the solvent ( $\text{m}^3 \text{ kmol}^{-1}$ ), and  $N_A$  is Avogadro's number ( $\text{kmol}^{-1}$ ). The molar volume of the solvent can then be calculated from the ratio [30]:

$$V_m = \frac{M}{d} \quad (12)$$

Where  $M$  is the molar mass of the solvent ( $\text{kg kmol}^{-1}$ ) and  $d$  the solvent density at a given temperature ( $\text{kg m}^{-3}$ ). Then, expressing eqn. (8) in terms of  $\sigma$  and  $F$  ( $\text{C kmol}^{-1}$ ), the following equation was obtained [31]:

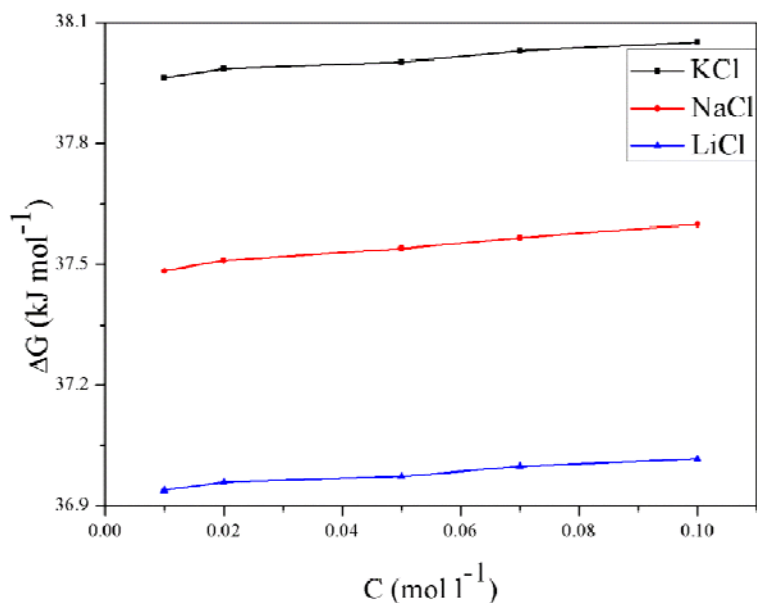
$$\Delta G = RT \left[ \ln \frac{|z|e_0 F}{6h(N_A)^{\frac{2}{3}}} + \frac{2 \ln V_m}{3} - \ln \sigma \right] \quad (13)$$

With this equation, the value of  $\Delta G$  can be calculated at any temperature provided the values of  $V_m$  and  $\sigma$  are known for this temperature. If the dependence of  $\Delta G$  on temperature is known, and the coefficients in the empirical equation for this dependence are known, then the value of  $\Delta S$  can be calculated by differentiating this equation with respect to temperature [30]:

$$\Delta S = - \frac{dG}{dT} \quad (14)$$

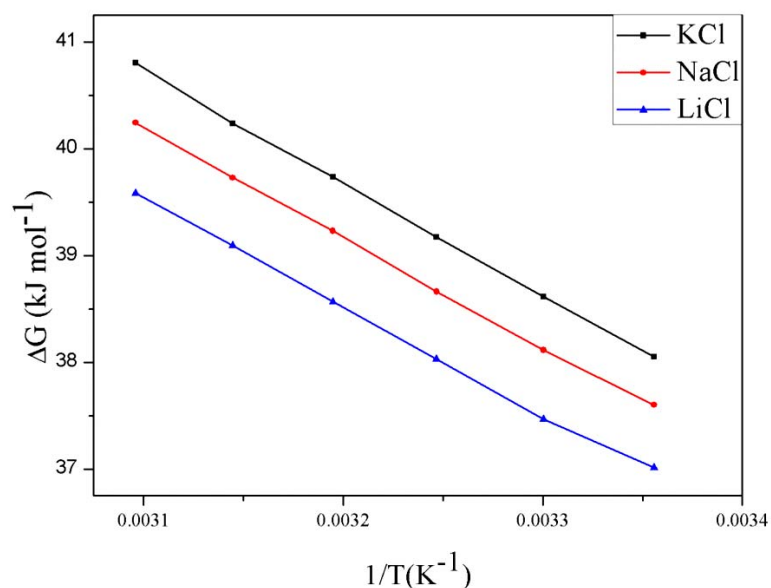
Using the values of  $\Delta S$  obtained at different temperatures, the values of  $\Delta H$  can be calculated by the well-known thermodynamic relation, eqn.(9). Using eqn.(13), the temperature dependence of the change of the Gibbs free energy for ionic migration were calculated.

Fig. 6 shows that the three curves are presented only that of  $\text{Li}^+$  has a minimum value.  $\Delta G$  increases with an increase in the concentration and follows the trend as  $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ .



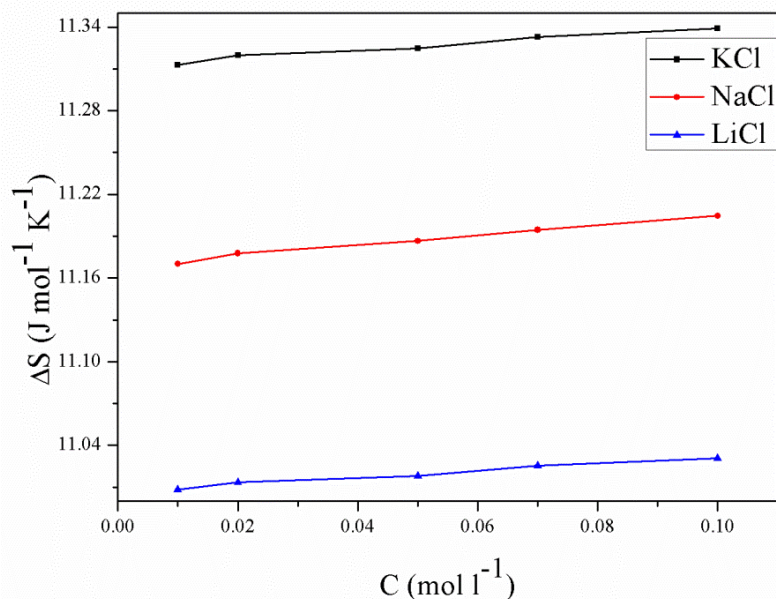
**Fig. 6.** Plot of Gibbs energy vs. concentration for the PZA composite membrane using 1:1 electrolytes at  $25 \pm 0.1$  °C

Fig. 7 shows that  $\Delta G$  regularly decreases with an increase in temperature due to the migration of a given ion in the solvent from one equilibrium state to another takesplace quickly when the ionic hydration-hydrate sphere is weaker, and thus a smaller number of hydrating solvent molecules will migrate together with the ion. Thus,  $\Delta G$  values for the electrolytes follow the sequence for the cations in the order  $K^+ > Na^+ > Li^+$ .



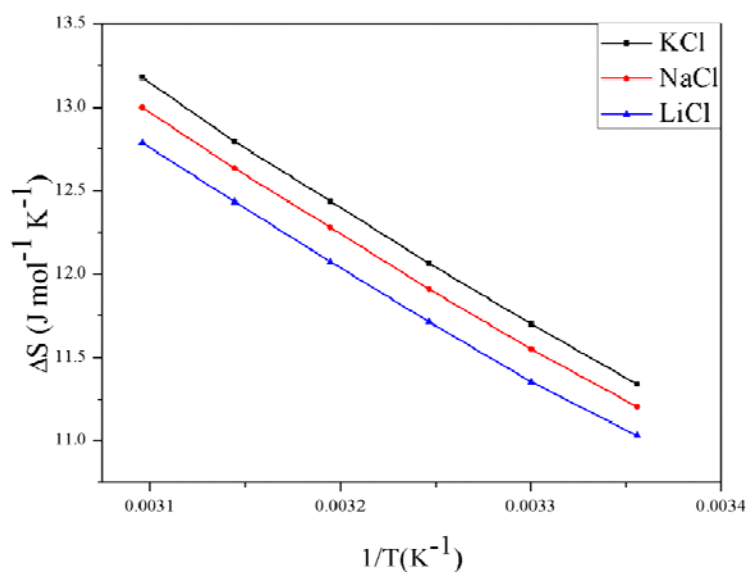
**Fig. 7.** Plot of Gibbs energy vs. temperature for the PZA composite membrane using 0.1 M of 1:1 electrolytes at  $(25-50) \pm 0.1$  °C

It is well known that the values of  $\Delta S$  for associated solvents such as water should be positive due to the transition of ions into the activated state is accompanied by the destruction of the solvent associates, and decrease of solvent structure. Fig. 8 shows that  $K^+$  has a maximum value. The  $\Delta S$  increases with an increase in the concentration and follows the trend as  $K^+ > Na^+ > Li^+$ . Thus positive value of  $\Delta S$  indicates that the diffusion of ion across the membrane generates a greater region of disorder [32].



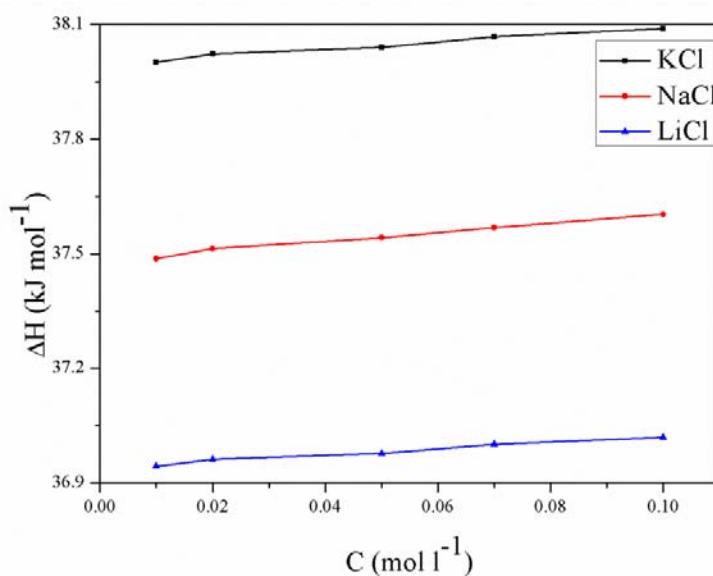
**Fig. 8.** Plot of entropy vs. concentration for the PZA composite membrane using 1:1 electrolytes at  $25 \pm 0.1$  °C

The values of  $\Delta S$  found to decrease with increasing of temperature because the solvent becomes less structured, which makes ionic movement easier. From Fig. 9, it can be stated that  $Li^+$  ion, which has the smallest radius, should be the least hydrated, whereas the  $K^+$  ion, which has the largest radius, should be the most hydrated. According to Zhitomirskii [31], it can be explained with an increase of the frequency at which water molecules are transported from co-ordination spheres of neighboring hydrated ions, thus leading to an increase in the hydration kinetics with increasing temperature. Therefore,  $\Delta S$  for 1-1 electrolytes were found to increase in the order  $K^+ > Na^+ > Li^+$ .



**Fig. 9.** Plot of entropy vs. temperature for the PZA composite membrane using 0.1 M of 1:1 electrolytes at  $(25-50) \pm 0.1$  °C

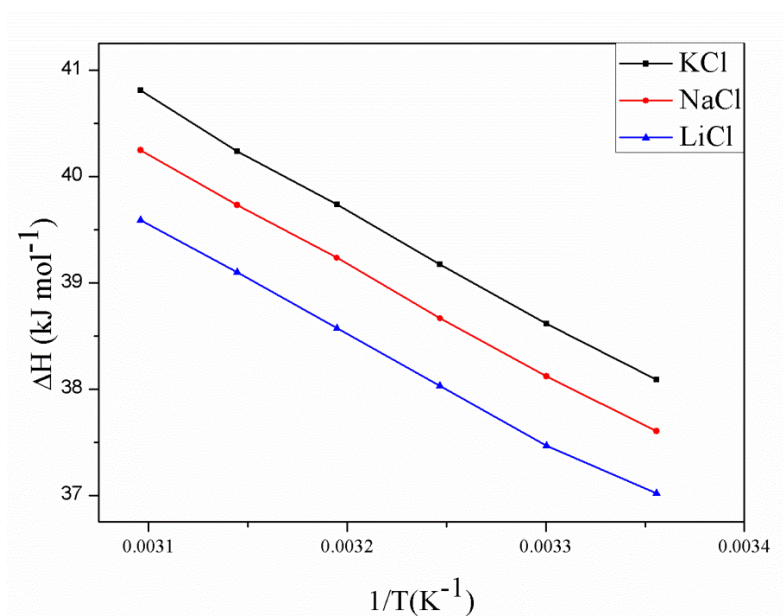
Fig. 10 shows that the value of  $\Delta H$  are positive in all of the cases, implying that the process of ion migration is energetically distributed because the ion must get through a certain energetic barrier. In all cases a increase of  $\Delta H$  with increasing electrolyte concentration was found and follows the trend  $K^+ > Na^+ > Li^+$ .



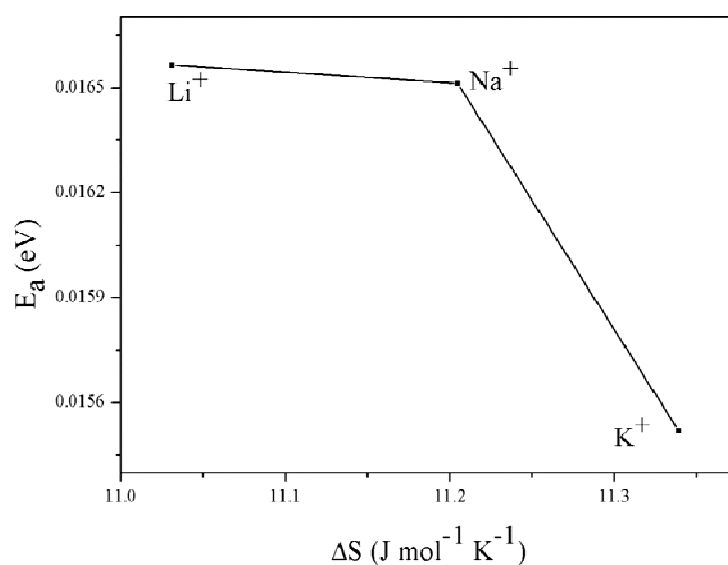
**Fig. 10.** Plot of enthalpy vs. concentration for the PZA composite membrane using 1:1 electrolytes at  $25 \pm 0.1$  °C

Fig. 11 shows that a decrease in the  $\Delta H$  values with increasing temperature is due to the temperature dependence of the electrolyte and follows the trend  $K^+ > Na^+ > Li^+$ . The values hardly differ even though different electrolytes were employed. The different slopes of the

straight lines can be explained by the different strength of the waters of hydration that are bound to the ions, 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 with the ion during translation.



**Fig. 11.** Plot of enthalpy vs. temperature for the PZA composite membrane using 0.1 M of 1:1 electrolytes at  $(25-50) \pm 0.1$  °C



**Fig. 12.** Plot of activation energy vs. entropy for the PZA composite membrane using 1:1 electrolytes at  $25 \pm 0.1$  °C

Fig. 12 shows that a system with a higher entropy changes  $\Delta S$  will require less energy of activation for its thermal dehydration. Such dependence was observed also for the thermal decomposition of other compounds [33-35].

#### 4. CONCLUSION

In conclusion, we report the promising conductivities of the PZA composite material. The present study was focussed on the measurement of conductivity. The conductivity of the membrane was investigated in the temperature range of  $(25-50)\pm 0.1^\circ\text{C}$  and different electrolyte concentration ranges ( $0.01 \leq C \text{ (M)} \leq 1$ ) using multi-meter. From the electrolyte concentration and temperature dependent conductivity studies, it was observed that the conductivity decreased with increasing electrolyte concentration and increased with increasing temperature. The activation energy increased with increase in concentration of the electrolyte. The values of  $\Delta G$  are positive in all of the cases, implying that the process of ion migration is energetically disturbed because the ion must get through a certain energetic barrier. The values of  $\Delta G$  increased with the increase of concentration and decreased with the increase of temperature and followed the sequence for the cations in the order  $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ . The value of both cases i.e.,  $\Delta H$  and  $\Delta S$  are also positive in nature and follows the same trend as  $\Delta G$ .

#### Acknowledgments

The authors acknowledge the North-West University and the PGM Group for instrumentation facility provided to carry out this research. Miss Simin Fatima is acknowledged for her nice cooperation. We thank an anonymous reviewer for constructive criticism on an earlier manuscript version.

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