Conductance Studies of Inorganic Precipitate Pb(IV) Tungstate Membrane Based on Non-Equilibrium Thermodynamics

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Abstract

The study of electrical conductance of parchment supported Pb(IV) tungstate membrane bathed in bi-univalent chlorides of magnesium, calcium and zinc solutions of different concentrations at different temperatures (25 to 50℃) has been measured. Absolute reaction rate theory has been applied to derive different thermodynamic parameters like Ea, ΔH^*, ΔG^* and ΔS^*. 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. The membrane was characterized by Scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) technique.

Keywords: *Pb(IV) tungstate membrane, Electrical conductance, Thermodynamic parameters, Membrane techniques.*

1. Introduction

The ion-exchange composite membranes find applications in various processes such as electro dialysis, desalination, diffusion, electro-deionization, membrane electrolysis, electrochemical synthesis, fuel cells, and storage batteries also. Therefore, they are useful in pollution control, energy saving, power generation, resource recovery, etc. [1-3]. The electrochemical characteristics and electrical conductance of the membrane depend on the nature of membrane forming materials, the structure of membrane and the concentration of the electrolytic solution in which the membrane is operated [4,5].

The electrochemical classification included the important parameters of the membrane such as water content nature, transport property, thickness, swelling, thermal and chemical stability, ion exchange capacity etc [6,7].

In this work, we describe the preparation of parchment supported Pb(IV) tungstate membrane and using the conductometric measurements to determine the conductivity values for different bi-univalent electrolytes at various concentrations. The selective inorganic precipitate membrane behavior has been discussed in terms of thermodynamic activation parameters evaluated by using the absolute reaction rate theory.

2. Materials and method

Na_2WO_4 (E. Merck, Mumbai, India), $Pb(NO_3)_2$ (E. Merck, Mumbai, India) and parchment paper (Amol Group of Companies Mumbai, India) were used to synthesis the inorganic precipitate membrane. All other reagents used were of analytical reagents grade. The bi-univalent chlorides of magnesium, calcium and zinc solutions were used for electrochemical characterization.

2.1. Membrane preparation

Parchment supported Pb(IV) tungstate inorganic precipitate membrane was prepared by the method of interaction as described by Ansari and coworkers [8-11]. To precipitate these substances in the interstices of parchment paper, a 0.2M solution of Na_2WO_4 was placed inside glass tube, to one end of which was tied

the parchment paper previously soaked in deionized water. The tube was suspended for 72 hours in a 0.2M solution of $Pb(NO_3)_2$. The two fresh solutions were interchanged later and kept for another seventy two hours. Thus, parchment paper and inorganic precipitate as a whole act as a synthetic membrane. The membrane thus prepared was washed many times with deionized water to wash free electrolytes.

2.2. Measurement of electrical conductance

The membrane was sealed between two half cells as described in our earlier communication [12]. The half cells were first filled with electrolyte solutions ($MgCl_2$, $CaCl_2$ and $ZnCl_2$) to equilibrate the membrane (Fig.1). The solutions were 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. Saturated calomel electrodes were used to establish electrical contacts. The membrane conductance was monitored on a direct reading conductivity meter 306 (Systronics) at a frequency of 103 Hz. All measurements were carried at 25, 30, 35, 40, 45 and 50 (±0.1°C). The electrolyte solutions were prepared from AR reagents in deionized water.

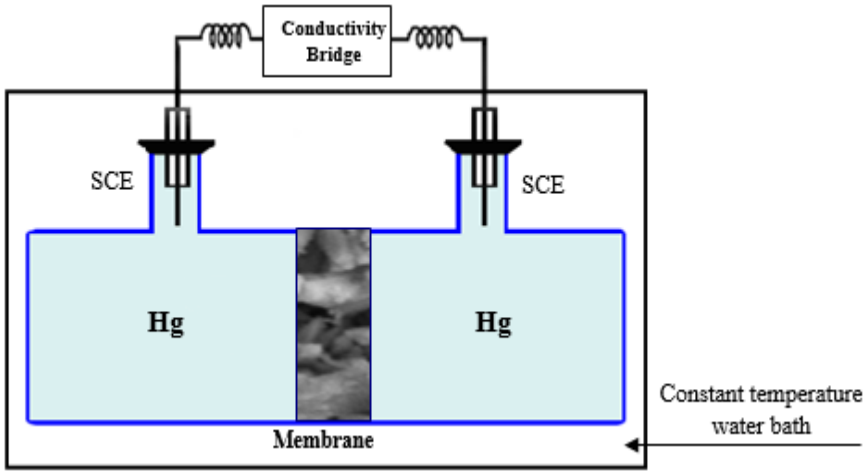


Fig. 1. Measurement of electrical conductance

2.3. Characterization of membrane

In order to judge the performance of the composite membrane, the complete physicochemical characterization has been done and this includes the determination of parameters like membrane water uptake, porosity, thickness, swelling etc. These influence the electrochemical properties of membrane [13].

2.3.1. Water uptake (% total wet weight)

The membrane was soaked in distilled water for 2 hour, blotted quickly with Whatsman filter paper to remove surface moisture and immediately weighted. These were further dried to a constant weight in vacuum over P_2O_5 for 24 hour. The water uptake (total wet weight) was calculated as follows

$$\%\ total\ wet\ weight = \left(\frac{W_w - W_d}{W_w}\right) x100$$

Where

Ww is the weight of the soaked or wet membrane and

Wd the weight of the dry membrane

2.3.2. Porosity

Porosity was determined as the volume of water incorporated in the cavities per unit membrane volume from the water uptake data

$$Porosity = \left(\frac{W_w - W_d}{AL\rho_w} \right)$$

Where A is the area of the membrane (cm^2). L the thickness of the membrane (cm) and ρ_w the density of water (g/cm^3).

2.3.3. Thickness

The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauze.

2.3.4. Swelling

Swelling was measured as the difference between the average thickness of the membrane equilibrated in 1M NaCl for 24 hour and the dry membrane.

2.3.5. Scanning electron microscopy studies

The characterization, pore structure, micro/macro porosity, homogeneity, thickness, cracks and surface morphology of Pb(IV) tungstate membrane was analyzed with SEM model phillips 515, USA. Gold Sputter coatings was carried out on the desired membrane sample at pressure 1 Pa.

2.3.6. Fourier transformed infrared studies

The FT-IR spectrum of parchment supported Pb(IV) tungstate membrane was done by Perkin-Elmer instrument model spectrum BX series Perkin Almer (USA) in the region 400-4400 cm^{-1}. The entrance and exit beams to the sample compartment were sealed with a coated KBr window and there was a hinged cover to seal it from the environment.

2.3.7. Thermogravimetric Analysis (TGA) studies

The degradation process and thermal stability of the membrane was investigated using thermogravimetric analyzer (Perkin Elmer, Pyris Diamond), under N_2 atmosphere (200 ml/min.) using a heating rate of 10℃ min^{-1} from 25℃ to 1100℃.

2.3.8. X-ray diffraction studies

The XRD image of the Pb(IV) tungstate membrane was recorded by Mini Flex-II X-ray diffractrometer (Rigaku Corporation) with CuKα.radiation.

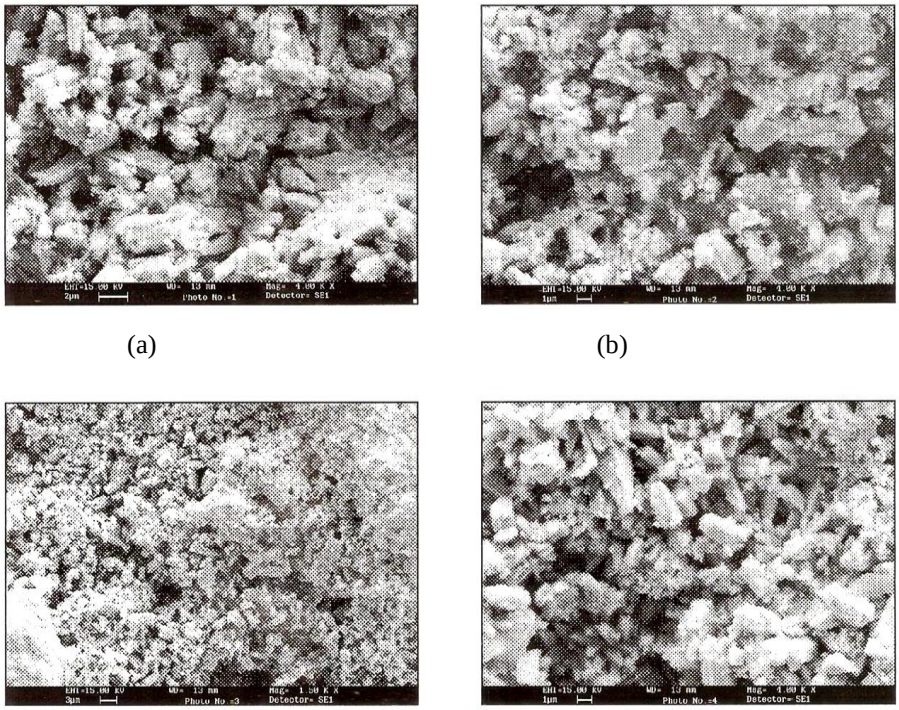
3. Results and discussion

The results of thickness, swelling, porosity and water content capacity of parchment supported Pb(IV) tungstate membranes are summarized in Table 1.

Table 1. Water content, Porosity, Thickness, and swelling Properties of Pb(IV) tungstate synthetic membrane

Water uptake as % Weight of Wet membrane	0.071
Porosity	0.114
Thickness(cm)	0.085
Swelling (%)	0.09

The SEM images of parchment supported synthetic membrane is shown in Fig. 2(a-d). SEM images appear to be composed of dense and loose aggregation of small particles and formed pores probably with the non-linear channel but no fully interconnected. Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various size.



(a) (b)

(c) (d)

Fig. 2(a-d). Scanning electron micrographs (SEM) of parchment supported Pb(IV) tungstate membrane

The FT-IR spectra for Pb(IV) tungstate membrane has been displayed in Fig. 3(a) by the blue spectra. The sample spectra has also been compared with Fluka library to find out possible structure of same membrane as displayed in Fig. 3(b) by red spectra.

On comparison it has been found that it shows the similarities with following compounds with percentage probability given in Table 2. Peak table with % transmission has also been given in Table 3.

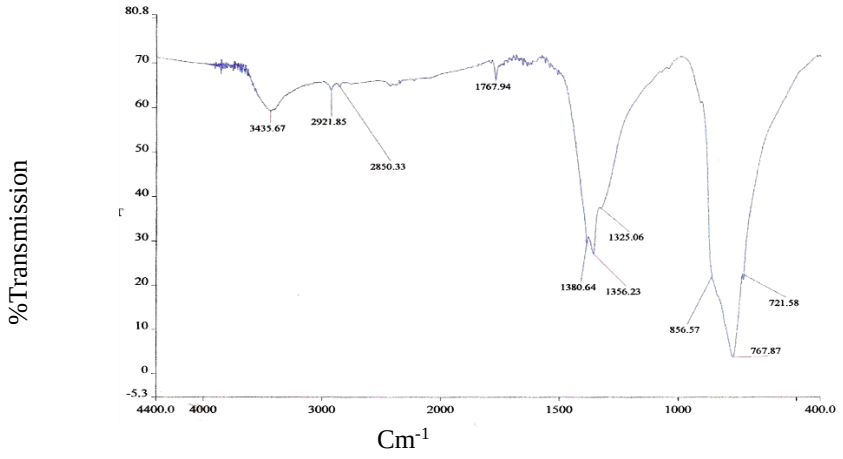


Fig. 3(a) FT-IR Spectra of parchment supported Pb(IV) tungstate synthetic membrane

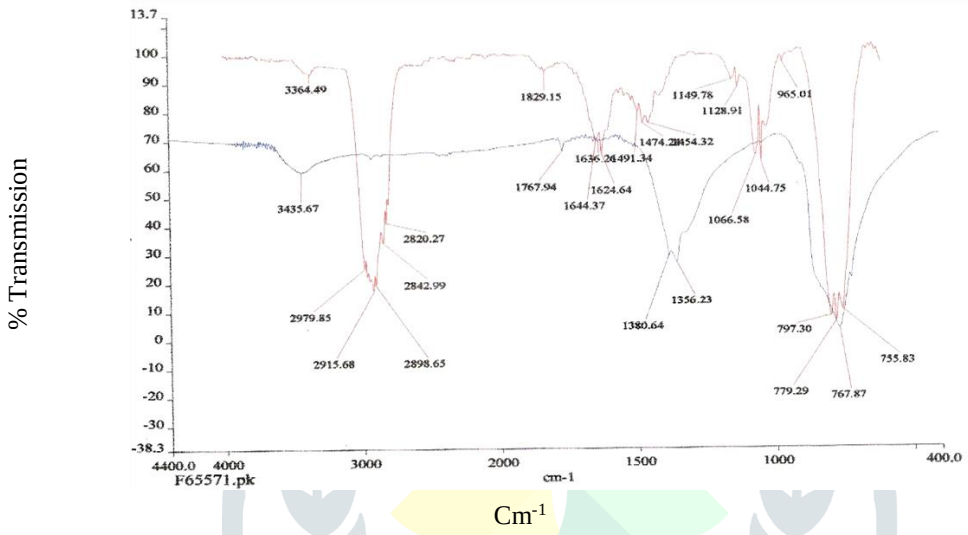


Fig. 3(b) FT-IR Spectra of parchment supported Pb(IV) tungstate membrane compared with Fluka Library

Table 2. Percentage structural probability of the Pb(IV) tungstate synthetic membrane

% Probability	Compound
0.447	Methylamine Anhydrous
0.422	1-bromonaphthalene
0.403	Chloral anhydrous
0.382	Carbon tetrachloride

Table 3. Peak table with % transmission of Pb(IV) tungstate synthetic membrane

Peak No.	Wave number (cm^{-1})	% Transmission
1	3435.67	59.17
2	17637.94	66.07
3	1356.23	27.03
4	767.37	3.79

The above studies shows that the parchment supported Pb(IV) tungstate membrane has the presence of IR active bands. This study will be helpful to assign the exact structure of the Pb(IV) tungstate membrane and then in turn to have its applications in the various field of practical interest.

The thermal stability of the Pb(IV) tungstate membrane was analyzed by TGA. The TGA curve measured under flowing nitrogen is reported in Fig. 4. TGA of the membrane material showed gradual weight loss of about 3% to 11% from 400℃ to 580℃ which may be due to the removal of external water molecules present at the surface of the membrane material. Further weight loss of 15% to 20% from 800℃ to 1000℃ indicating the start of condensation due to the removal of the lattice water from the material.

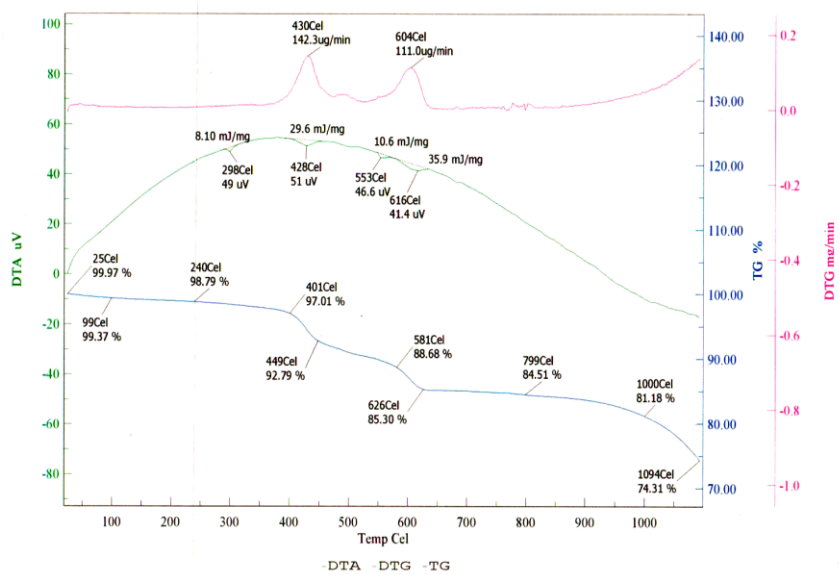


Fig. 4. TGA curve (blue spectra) of the parchment supported Pb(IV) tungstate membrane

Fig. 5. shows X-ray diffraction spectrum of the Pb(IV) tungstate membrane. The material recorded in powdered sample exhibited some sharp peaks in the spectrum (2ϑ range) shows semi-crystalline nature of the material.

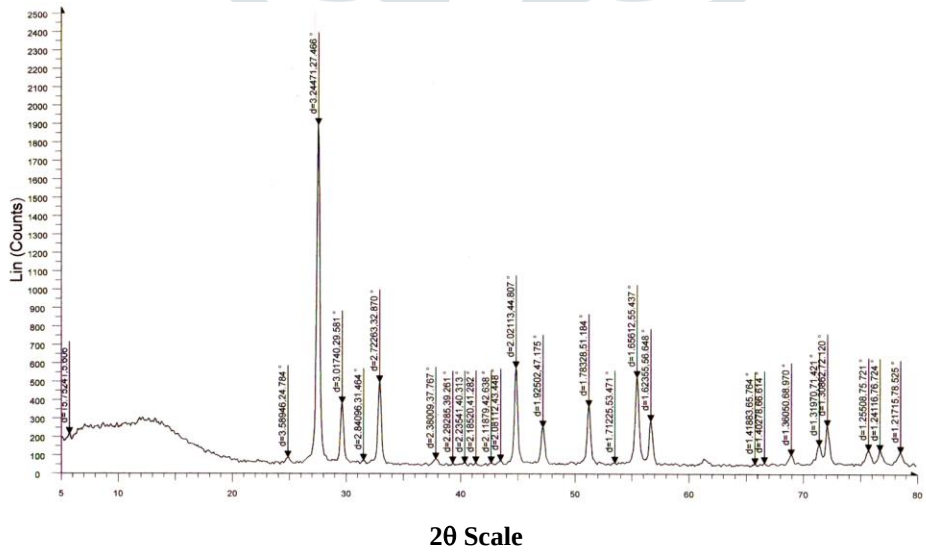


Fig. 5. XRD pattern of parchment supported Pb(IV) tungstate membrane

Experimental values of Electrical Conductance X10^3 (S m $^{-1}$) across parchment supported Pb(IV) tungstate membrane of various bi-univalent electrolytes at various temperature ranges 25, 30, 35, 40, 45 and

50 (±0.1°C) as shown in Table 4 to 6. The values are relatively more dependent on the concentration of the electrolytes within the membrane as shown in Fig. 6 to 8.

Table 4. Experimental values of Electrical Conductance X10^3 (S m^{-1}) for $MgCl_2$ electrolyte at various temperature (25 to 50) ± 0.1°C across parchment supported Pb(IV) tungstate membrane

Electrolyte	Conc. (mol/L)	Temperature (°C)					
		25	30	35	40	45	50
$MgCl_2$	0.1	10.26	10.67	10.96	11.82	12.82	12.98
	0.5	6.49	7.83	7.93	8.67	9.63	10.26
	0.05	5.59	5.99	6.02	7.13	7.72	8.25
	0.02	4.66	4.95	5.01	5.45	5.80	6.98
	0.01	3.95	4.29	4.60	4.79	5.20	6.89

Table 5. Experimental values of Electrical Conductance X10^3 (S m^{-1}) for $CaCl_2$ electrolyte at various temperature (25 to 50) ± 0.1°C across parchment supported Pb(IV) tungstate membrane

Electrolyte	Conc. (mol/L)	Temperature (°C)					
		25	30	35	40	45	50
$CaCl_2$	0.1	11.28	11.69	11.98	12.82	13.82	13.98
	0.5	7.52	8.87	8.97	9.67	10.63	11.26
	0.05	6.60	6.96	7.78	8.13	8.72	9.25
	0.02	5.68	5.78	6.45	6.45	6.80	7.98
	0.01	4.98	5.54	5.65	5.89	6.50	7.97

Table 6. Experimental values of Electrical Conductance X10^3 (S m^{-1}) for $ZnCl_2$ electrolyte at various temperature (25 to 50) ± 0.1°C across parchment supported Pb(IV) tungstate membrane

Electrolyte	Conc. (mol/L)	Temperature (°C)					
		25	30	35	40	45	50
$ZnCl_2$	0.1	12.30	12.72	12.92	13.85	14.87	14.99
	0.5	8.55	9.89	9.98	10.66	11.67	12.30
	0.05	7.67	7.98	8.83	9.54	9.87	10.45
	0.02	6.70	6.80	7.50	7.49	7.88	8.99
	0.01	5.99	6.59	6.69	6.98	7.70	8.98

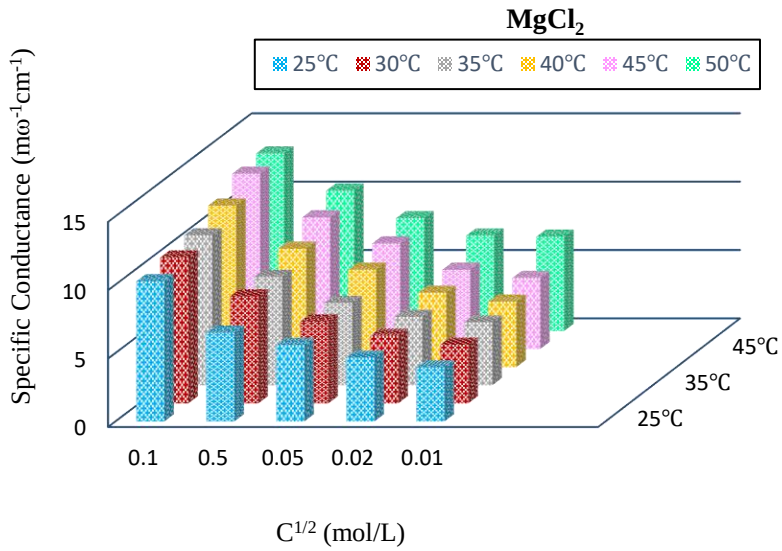


Fig. 6. Plots of specific conductance ($m\Omega^{-1}cm^{-1}$) against square root of concentrations for $MgCl_2$ at different temperatures across Pb(IV) tungstate membrane

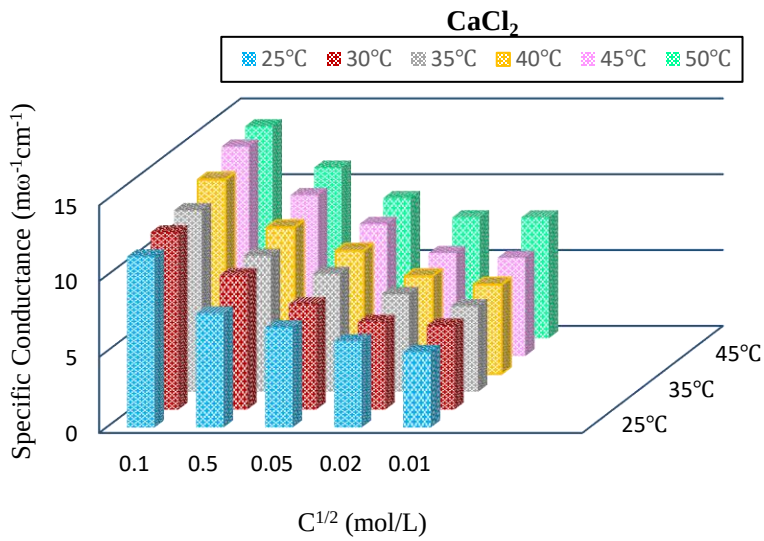


Fig. 7. Plots of specific conductance ($m\Omega^{-1}cm^{-1}$) against square root of concentrations for $CaCl_2$ at different temperatures across Pb(IV) tungstate membrane

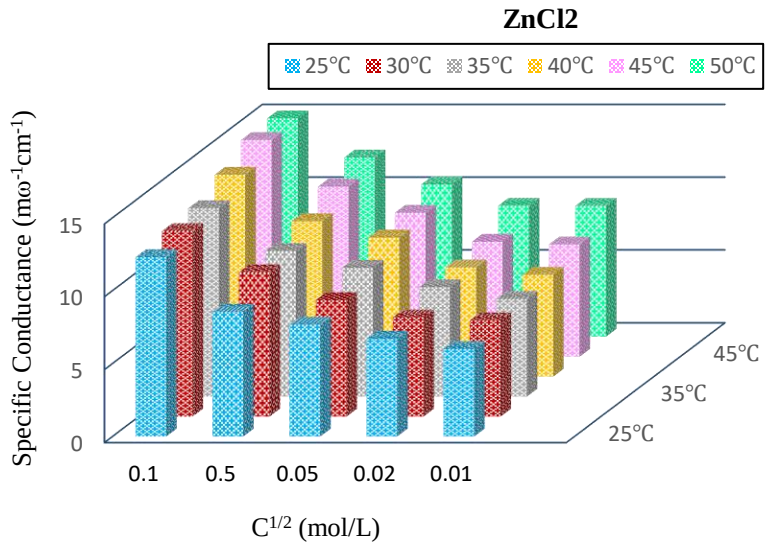


Fig. 8. Plots of specific conductance ($m\Omega^{-1}cm^{-1}$) against square root of concentrations for $ZnCl_2$ at different temperatures across Pb(IV) tungstate membrane

These values 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 [14] for nylon membranes with various bi-univalent electrolytes. The sequence of membrane conductance for the ions under the same condition is $Zn^{++} > Ca^{++} > Mg^{++}$, similar to their ionic radii order. Similar behaviour was observed by several investigators for certain synthetic membranes [15,16]. This sequence indicates that the size of the ions is the major factor in the diffusion process.

Table 7 shows that the activation energy decreases with increase in concentration of the bathing bi-univalent electrolyte solution and that for different electrolytes at a particular concentration it follows the order: $Ea_{Zn^{++}} > Ea_{Ca^{++}} > Ea_{Mg^{++}}$ analogous to the sequence of crystallographic radii of the metal cations. When the penetrant moves in a polymer substance containing relatively small amount of water, it smotion 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 enought to accommodate a penetrant species [17].

Table 7. Calculated values of Activation Parameters for bi-univalent electrolytes through Pb(IV) tungstate membrane

Electrolyte	Conc.(mol/L)	E_a (KJ/mole)	ΔH^*(KJ/mole)	ΔG^*(KJ/mole)	$-\Delta S^*$($JK^{-1}mol^{-1}$)
$ZnCl_2$	0.1	11.05	7.99	80.17	318.17
	0.01	12.99	11.29	86.16	330.30
$CaCl_2$	0.1	9.18	6.45	79.37	319.17
	0.01	12.99	11.17	88.18	335.22
$MgCl_2$	0.1	7.35	4.56	79.56	320.01
	0.01	12.43	10.17	87.27	335.04

Table 8 shows that an increase of activation energy with an increase of crystallographic radius confirms the applicability of Kumins [18] impacts for parchment supported inorganic precipitate membrane systems.

Table 8. Relation between Crystallographic radius and activation energy of salts

Ion	Crystallographic radii (Å)	Energy of activation (KJ/mole)
Zn^{++}	2.41	10.97
Ca^{++}	1.98	8.16
Mg^{++}	1.70	6.98

The thermodynamic parameters, ΔH^*, ΔS^* and ΔF^*, and have been determined using the theory of absolute reaction rates. Following Eyring [19, 20].

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

where π is the membrane conductance, h is the Planck constant, R is the gas constant, N is the Avogadro number and T is the absolute temperature, ΔG^* is the free energy of activation for the diffusion of ions and is related to the enthalpy ΔH^* by the equation

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (2)$$

ΔH^* is related to Arrhenius energy of activation E_a, given by

$$E_a = \Delta H^* + RT \qquad (3)$$

A plot of log π Nh/RT Versus 1/T shown in Fig. 9. The slope of which give the energy of activation as required by Arrhenius equation. The experimental values gives a straight line, the slope and the intercept of which gives the value for ΔH^* and ΔS^* as demanded by equation (1). This justifies the applicability of equation (1) to the system under investigation. The derived values of ΔH^* and ΔS^* were then used to get the value of ΔG^* and Ea using equations (2) and (3). The values of various thermodynamic activation parameter, Ea, ΔH^*, ΔG^* and ΔS^* derived in this way, for diffusion of various electrolytes in the synthetic membrane are given in Table 7.

These results indicate that the electrolyte permeation gives rise to negative values of ΔS^*. In addition to this the values of ΔS^* are more negative for the membranes prepared at higher pressure. Amongst the cations order of ΔS^* is given below:

$$Zn^{++} > Ca^{++} > Mg^{++}$$

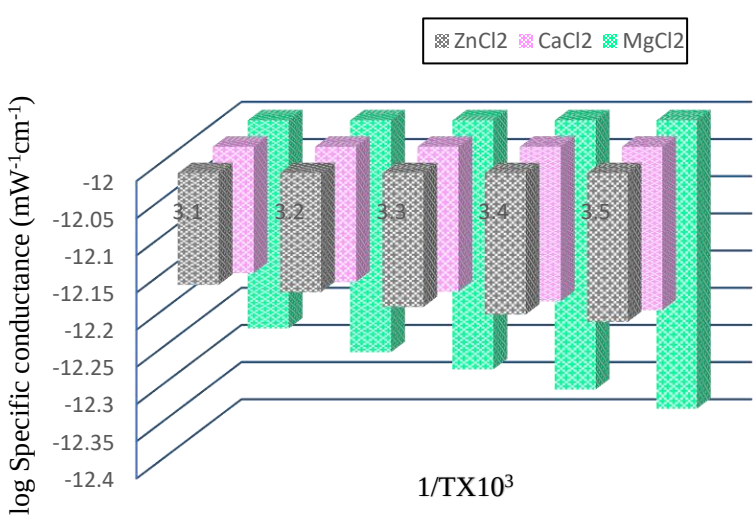


Fig. 9. Arrhenius plots of specific conductance

4. Conclusion

The parchment supported Pb(IV) tungstate membrane was successfully synthesized by using ion-interaction method. The electrical conductance of ions across synthetic membrane were measured with bi-univalent electrolytic solutions of different concentrations at various temperature ranges (25 to 50℃) has been measured. The conductance order of various electrolytes were found to follow the sequence for the cations: $Zn^{++} > Ca^{++} > Mg^{++}$. Negative ΔS^* values suggest that the partial immobilization of ionic species takes place, most probably due to the interstitial permeation and ionic interaction with the fixed charge group on the membrane skeleton.

Acknowledgement

The authors are thankful to the Principle of the college for providing the necessary research facilities.

References

1. Gohil GS, Nagarale RK, Binsu VV, Shahi VK, Preparation and characterization of monovalent cation selective sulfonated poly(ether ether ketone) and poly(ether sulfone) composite membranes. J Colloid Interface Sci, 298, 845-853 (2006)
2. Tauseef Ahmad Rangreez, Inamuddin, Synthesis and characterization of graphene Th(IV) phosphate composite cation exchanger: analytical application as lead ion-selective membrane electrode, Desalination and Water Treatment, 1–10 (2016)
3. Mohd Arsalan, Mohammad Mujahid Ali Khan, Rafiuddin, Thermodynamic evaluation and electrochemical parameters of PVC-based ion-exchange nickel tungstate composite membrane and their potential applications, Desalination and Water Treatment, 1-9 (2014)
4. K. Miyazaki, Y. Kato, T. Matsui, S. Hayashi, Y. Iriyama, T. Fukutsuka, T. Abea Z. Ogumi, Formation of "fuzzy" phases with high proton conductivities in the composites of polyphosphoric acid and metal oxide nanoparticles, Phys. Chem. Chem. Phys., 14, 11135-11138 (2012)
5. Zeid Abdullah ALOthman, Mohammad Mezbaul Alam, Mu. Naushad, Rani Bushra, Electrical Conductivity and Thermal Stability Studies on Polyaniline Sn(IV)tungstomolybdate Nanocomposite CationExchange Material: Application as Pb(II) Ion-Selective Membrane Electrode, Int. J. Electrochem. Sci., 10, 2663 – 2684 (2015)
6. N. Asano, M. Aoki, S. Suzuki, K. Miyatake, H. Uchida, M. Watanabe, Aliphatic/aromatic polyimide ionomers as a proton conductive membrane for fuel cell applications, J. Am. Chem. Soc., 128, 1762–1769 (2006)
7. Murali Manohar, Arindam K. Das, V.K.Shahi, Alternative preparative route for efficient and stable anion-exchange membrane for water desalination by electrodialysis, Desalination 413, 101–108 (2017)
8. Mohd Ayub Ansari, Manoj Kumar, Ashok Kumar, Preeti Shrivastava and R.S. Kushwaha, Studies of membrane selectivity from electrical potential and conductivity measurements, J. Ind. Council of Chem., 22(2), 23-31 (2005)
9. Mohd Ayub Ansari, Manoj Kumar, Neelam Singh, K.S. Dadoriya, R.S. Kushwaha an Shahanaz Ayub, Ion transport studies through polystyrene based model membrane: conductance data and absolute reaction rate theory, Adv. Appl. Sci. Res., 3 (1), 251-260 (2011)
10. Mohd. Rashid, Sher Ali and Mohd.Ayub Ansari, Synthetic, characterization and conductance studies of inorganic precipitate synthetic membranes, J. Applicable Chemistry, 2 (4), (2013) 738-747 (2013)
11. Mohd. Rashid, Sher Ali and Mohd. Ayub Ansari, Bi-ionic potential studies on parchment supported synthetic membranes, Der Chimica, Sinica, 4 (4), 97- 106 (2013)
12. Kushwaha, R.S. and Ansari, M.A., Preparation of parchment supported nickel and cobalt phosphate membranes and their studies as ion sensor with special reference to phosphate ion. Progressive Research. 3 (1), 73-75 (2008)

13. M.M.A. Khan, Rafiuddin, Inamuddin, Electrochemical characterization and transport properties of polyvinyl chloride based carboxymethyl cellulose Ce(IV) molybdophosphate composite cation exchange membrane, J. Ind. Eng. Chem. 18, 1391–1397 (2012)
14. Iijima, T.; Obara, T.; Isshiki, M., Sekj, T. and Adachi, K.J. (1978). Colloid Interface Sci., 63, 421 (1978)
15. Kushwaha, R.S.., Ansari, M.A., Singh, Kumar, M. and M.N. Beg., Synthesis of poly-styrene based nickel phosphate membranes and evaluation of membrane parameters to test the membrane potential theories. J. Ind. Chem. Soc., 87 (4), 471-479 (2010)
16. Ansari, M.A., Kumar Manoj, Singh, N., Dadoria, K.S., Kushwaha, R.S. and Ayub, S., Ion transport studies through polystyrene-based model membrane: conductance data and absolute reaction rate theory, Adv. Appl. Sci. Res., 3(1), 251-260 (2011)
17. Asif Ali Khan, Mohd Quasim Khan and Rizwan Hussain, Determination of Cd2+ in aqueous solution using polyindole–Ce(IV) vanadophosphate conductive nanocomposite ion-selective membrane electrode, Mater. Res. Express 4, 095024 (2017)
18. C.A. Kumins, T.K. Kwei, J. Crank, GS. Park Diffusion in Polymers, Academic Press, New York, (1968)
19. Glasstone, S., Laidler, K.J. and Eyring, H. (1941). The Theory of Rate Processes (McGraw Hill, New York), 525-544 (1941)
20. Barrer, R.M.; Bartholomew, R.F. and Res., L.V.C., J. Phys. Chem., Solids, 21, 12 (1961)