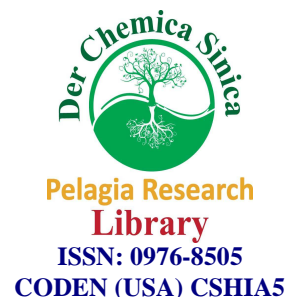




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### Effect of temperature on membrane potential and evaluation of thermodynamic parameters of parchment supported silver thiosulphate

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#### ABSTRACT

Membrane potentials for silver thiosulphate parchment supported membrane at different temperatures (30-60°C) have been measured. Experimental results were analyzed on the basis of the Kobatake equation. An increase with temperature of mobility ratio of the ions in the membrane phase ( $u_+/u_-$ ) has been found and the following order exists:  $NH_4Cl > KCl > NaCl$ . The activation thermodynamics parameters; enthalpy of activation  $\Delta H^\ddagger$ , entropy of activation  $\Delta S^\ddagger$  and free energy of activation  $\Delta G^\ddagger$ , have been estimated. The values of  $\Delta S^\ddagger$  are found to be negative indicating that diffusion takes place with partial immobilization in the membrane phase

**Keywords:** Silver Thiosulphate Membrane, Membrane Potential, Thermodynamic Parameters

#### INTRODUCTION

Transport processes occurring across artificial membranes separating different salts solutions are of great interest to chemists, chemical engineers, and biologists. Chemists and chemical engineers would like to understand the mechanism of transport so that with the knowledge so gained they would be able to fabricate membranes of any desired property or properties. Biologists, however, would like to use them as models for the physiological membranes to understand the behavior of complex cell membranes [1].

Several membranes have been prepared using inorganic salts. However these inorganic membranes have sufficiently low chemical stability in acidic and alkaline medium due to dissolution of inorganic phosphate into inorganic salt [2].

Different studies on permeability, permselectivity, and fixed charge density of various inorganic precipitate membranes have provided reasonably clear picture of the functioning of these membranes in contact with simple electrolyte solutions [3-18].

In this work, membrane potentials through silver thiosulphate parchment supported membrane for a wide interval of concentrations and different temperatures have been studied. The results have been analyzed by the Kobatake equation for the membrane potential [19]. The activation energy and the mobility ratio of ions in the membrane have also been obtained.

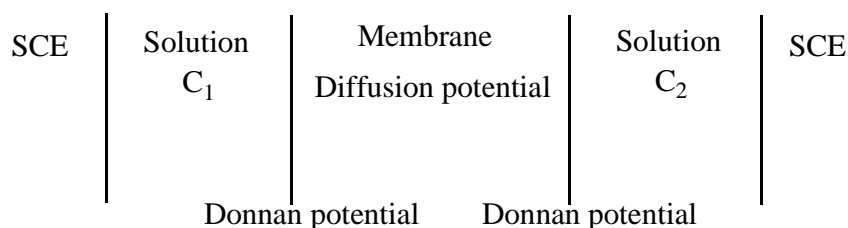
## MATERIALS AND METHODS

**Preparation of Membrane**

All the reagents used were of AR grade (BDH) and their solutions were prepared in doubly distilled water. Parchment supported silver thiosulphate membrane was prepared by the method of interaction described by Siddiqi *et al.* [3-6]. First parchment (Supplied by M/s Baird and Tatlock London Ltd.) was soaked in distilled water for about two hours and then tied to the flat mouth of a beaker containing 0.2 M silver nitrate solution. This was suspended for 72 hours in a 0.2 M sodium thiosulphate solution at room temperature. The two solutions were interchanged and kept for another 72 hours. In this way fine deposition of silver thiosulphate was obtained on the surface of parchment paper. The membrane thus obtained was well washed with deionized water for the removal of free electrolytes. The membrane was then cut into a circular disc form and was clamped between two half cells of an electrochemical cell. The membrane before the measurements had been aged by about 24 hrs immersion in 1 M in the testing electrolyte.

**Membrane Potential Measurements**

The potential developed by setting up a concentration cell of the type described by Siddiqi *et al.* [7]. The membrane potential was obtained by taking the same electrolyte at different concentrations on the two sides of the membrane, such that the concentration ratio  $\sigma = 10$ . The potentials were monitored by Knick Digital Potentiometer (No. 646). All measurements were carried out using a water thermostat at different temperatures (30-60°C). The solutions were vigorously stirred by a pair of magnetic stirrer to be maintained uniform in both the half cells. The uni-univalent electrolytes examined were sodium chloride, potassium chloride, and ammonium chloride. The salt solutions were prepared from AR reagents (BDH) without further purification and using doubly distilled water

**Nomenclature**

$E_m$  : Membrane Potential in millivolts

$u_+$  and  $u_-$  : Mobilities of cation and anion, respectively, in the membrane

$C_1$  and  $C_2$  : Concentrations of the electrolyte solutions on either side of the membrane

$X$  : Charge density expressed in equivalents per liter

$R$  : Molar gas constant

$T$  : absolute temperature of the system

$F$  : Faraday constant

$K$  : Constant depend on the viscosity of the solution and structural details of the membrane

$\alpha$  and  $\beta$  : Parameters independent of salt concentration

$\Delta E_{mr}$  : Reduced membrane potential

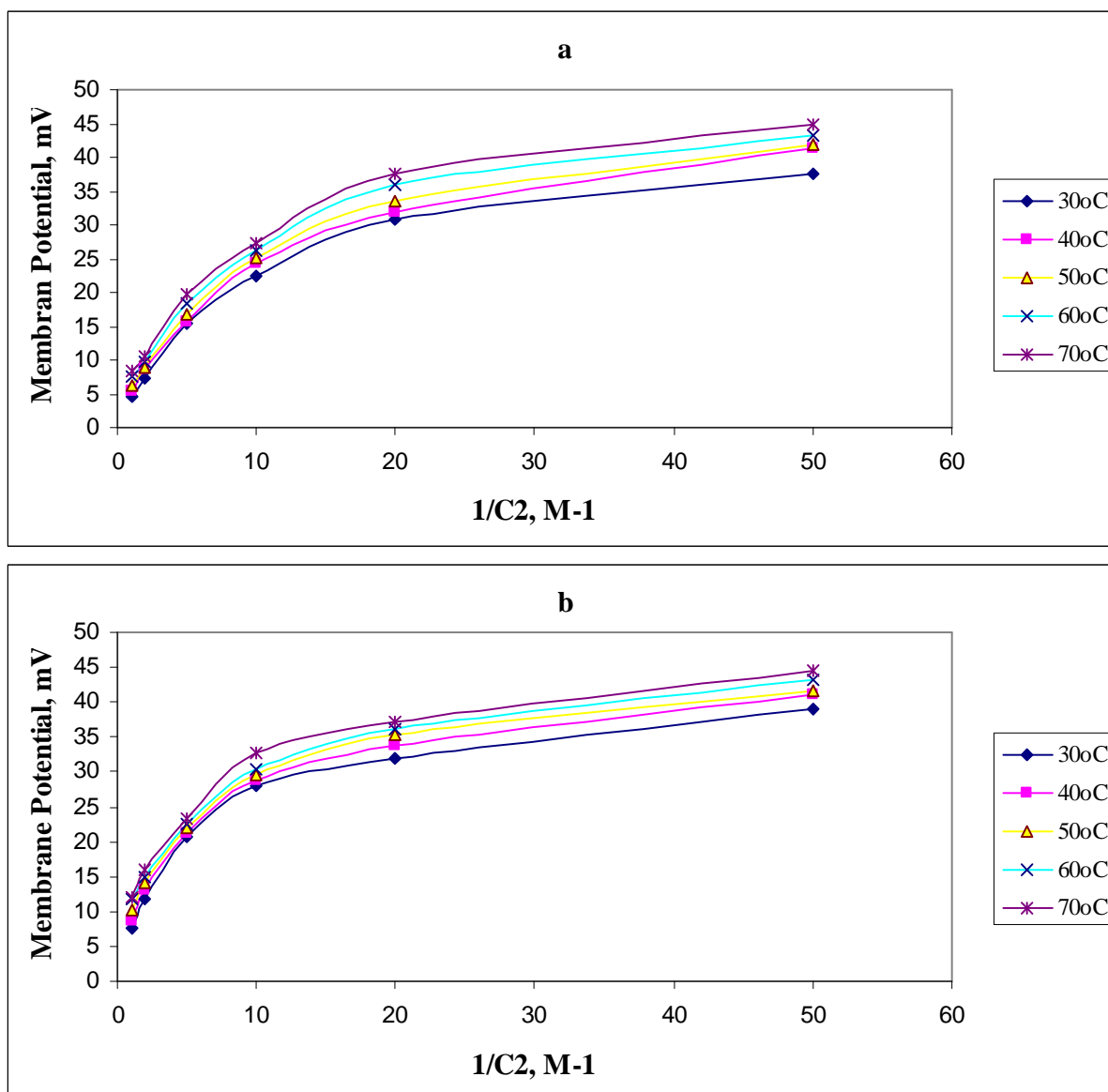
$$\sigma = \frac{C_2}{C_1}$$

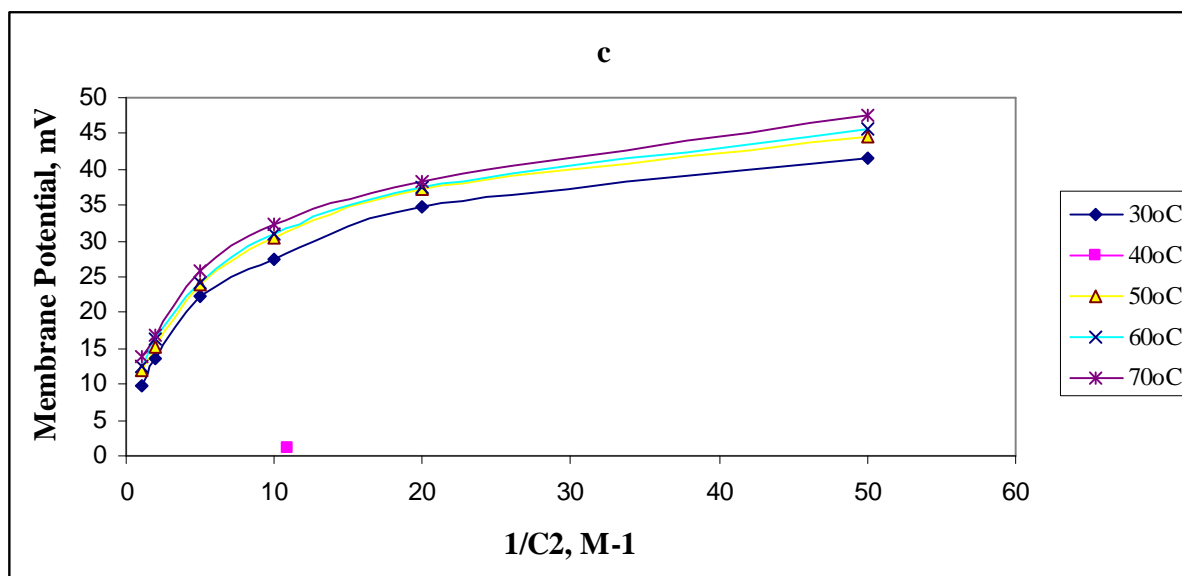
$t_{-app}$  : Apparent transference number for co-ion in a negatively charged membrane

## RESULTS AND DISCUSSION

Membrane potentials ( $\Delta E_m$ ) through silver thiosulphate membrane for a wide interval of concentration and different temperatures have been studied. The results have been analyzed by the Kobatake equation for membrane potential. This equation shows a relationship between the membrane potential and three parameters:  $X$ ,  $\alpha$ , and  $\beta$  which can be evaluated from experimental values. The parameter  $\beta$  is related to the fixed charge density in the membrane and a factor which depends on the viscosity of the solution and the structural details of the membrane while the parameter  $\alpha$  is related to mobilities of cations and anions. Therefore, the Kobatake equation could be used to elucidate if the variations with temperature are due to the electrolyte solution or to change in the membrane structure. The experimentally determined membrane potential values across silver thiosulphate membrane in contact with different concentrations of various 1:1 electrolytes at different temperatures are shown in Figures 1a, 1b, 1c.

Figure 1 Membrane Potential vs.  $\log(1/C_2)$  in contact with different concentrations of: (a) NaCl, (b) KCl, and (c)  $\text{NH}_4\text{Cl}$





The values of apparent transference number of co-ion calculated from the membrane potential measurements and using the Nernst equation (1) are given in Tables 1a, 1b, and 1c:

$$\Delta E_{mr} = (1 - 2 t_{-app}) \ln \sigma \tag{1}$$

Table 1 Apparent transference number of co-ions for various electrolytes at different concentrations

(a) NaCl

(C <sub>2</sub> /C <sub>1</sub> ) M	t <sub>app</sub>				
	30°C	40°C	50°C	60°C	70°C
1.0/0.1	0.463	0.457	0.452	0.443	0.439
0.5/0.05	0.438	0.431	0.430	0.426	0.422
0.2/0.02	0.371	0.373	0.369	0.360	0.355
0.1/0.01	0.315	0.305	0.304	0.301	0.299
0.05/0.005	0.244	0.243	0.239	0.228	0.223
0.02/0.002	0.186	0.167	0.173	0.172	0.169

(a) KCl

(C <sub>2</sub> /C <sub>1</sub> ) M	t <sub>app</sub>				
	30°C	40°C	50°C	60°C	70°C
1.0/0.1	0.437	0.431	0.421	0.411	0.412
0.5/0.05	0.403	0.395	0.389	0.387	0.383
0.2/0.02	0.328	0.328	0.328	0.329	0.330
0.1/0.01	0.266	0.268	0.269	0.270	0.259
0.05/0.005	0.234	0.228	0.224	0.226	0.226
0.02/0.002	0.176	0.170	0.175	0.172	0.172

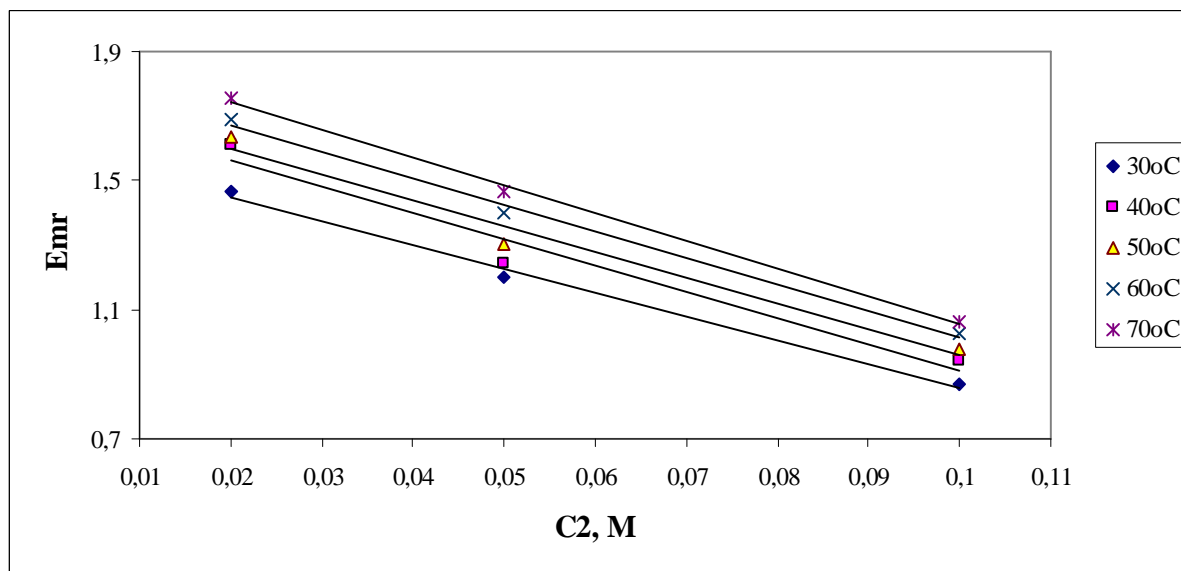
(a) NH<sub>4</sub>Cl

(C <sub>2</sub> /C <sub>1</sub> ) M	t <sub>app</sub>				
	30°C	40°C	50°C	60°C	70°C
1.0/0.1	0.418	0.412	0.406	0.405	0.399
0.5/0.05	0.386	0.384	0.381	0.376	0.377
0.2/0.02	0.314	0.316	0.314	0.316	0.311
0.1/0.01	0.271	0.266	0.263	0.266	0.263
0.05/0.005	0.211	0.212	0.211	0.215	0.219
0.02/0.002	0.155	0.155	0.152	0.155	0.150

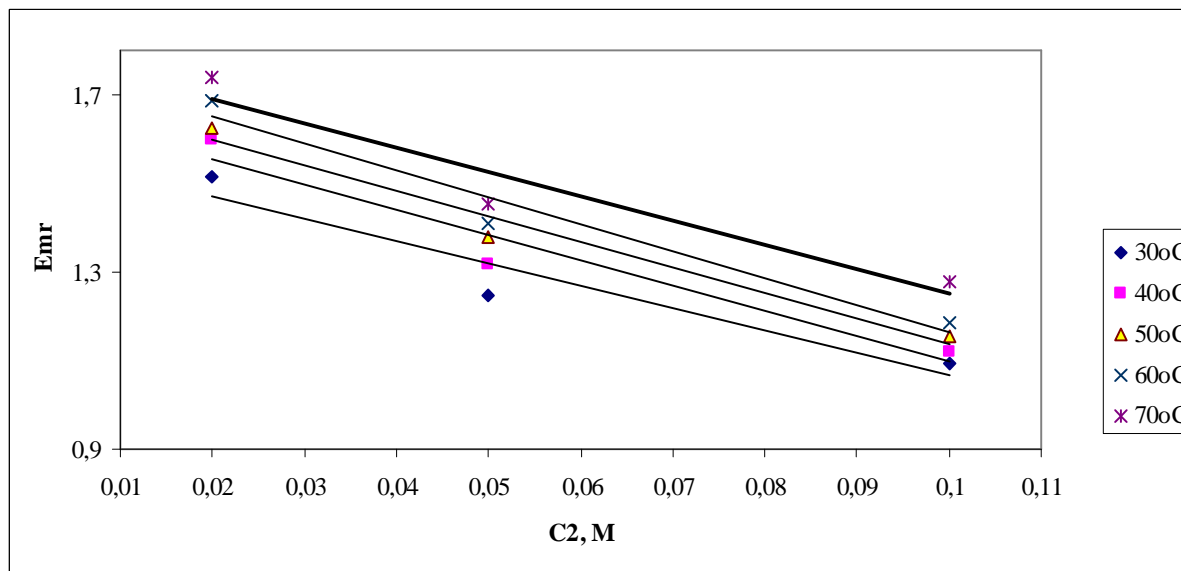
In Figures 2a, 2b, and 2c,  $|\Delta E_{mr}|$  versus  $C_2$  for low external concentrations at different temperatures has been drawn. The value of intercept is equal to  $(1/\beta) \ln \sigma$  (Equation 2), from which  $\beta$  may be evaluated at each given temperature:

$$|\Delta E_{mr}| = \left(\frac{1}{\beta}\right) \ln \sigma - \left(\frac{\sigma - 1}{\alpha\beta\sigma}\right) \left(1 + \frac{1}{\beta} - 2\alpha\right) \left(\frac{C_2}{X}\right) \tag{2}$$

(a) NaCl



(b) KCl



(c) NH<sub>4</sub>Cl

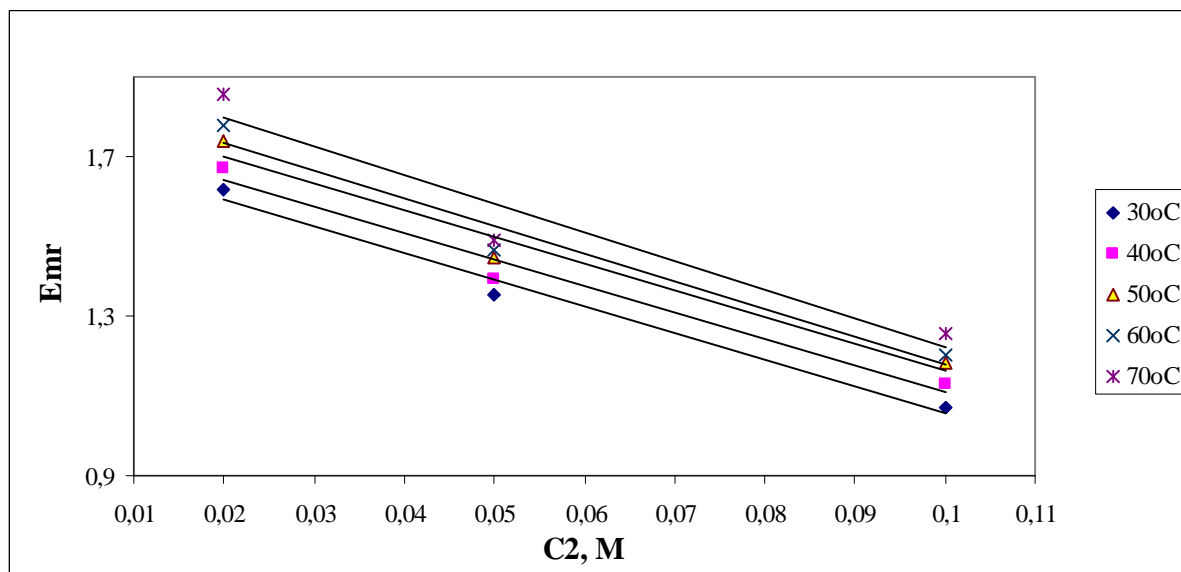
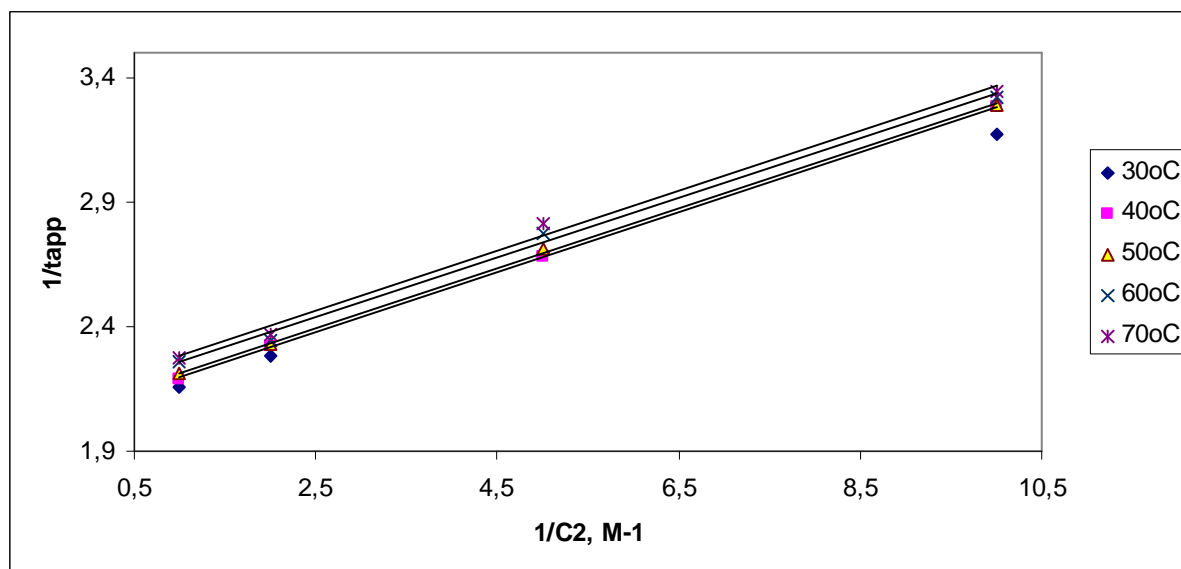


Figure 2 E<sub>mr</sub> vs C<sub>2</sub> in contact with different electrolytes (at low concentrations)

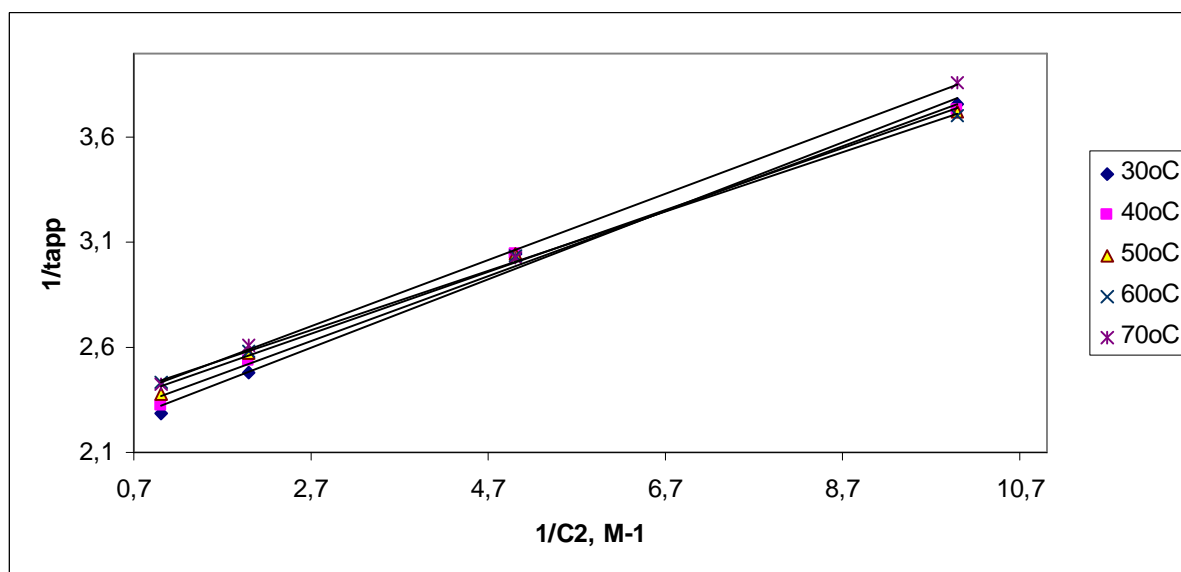
Figures 3a, 3b, and 3c show 1/t<sub>app</sub> as a function of 1/C<sub>2</sub> at high values of the salt concentration. From the intercept of these straight lines (Equation 3), the value of α at each temperature was determined.

$$\frac{1}{t_{app}} = \frac{1}{1-\alpha} \left[ \frac{(1+\beta-2\alpha\beta)(\sigma-1)\alpha}{2(1-\alpha)^2 \ln \sigma} \right] \left( \frac{X}{C_2} \right) \quad (3)$$

(a) NaCl



(b) KCl



(c) NH<sub>4</sub>Cl

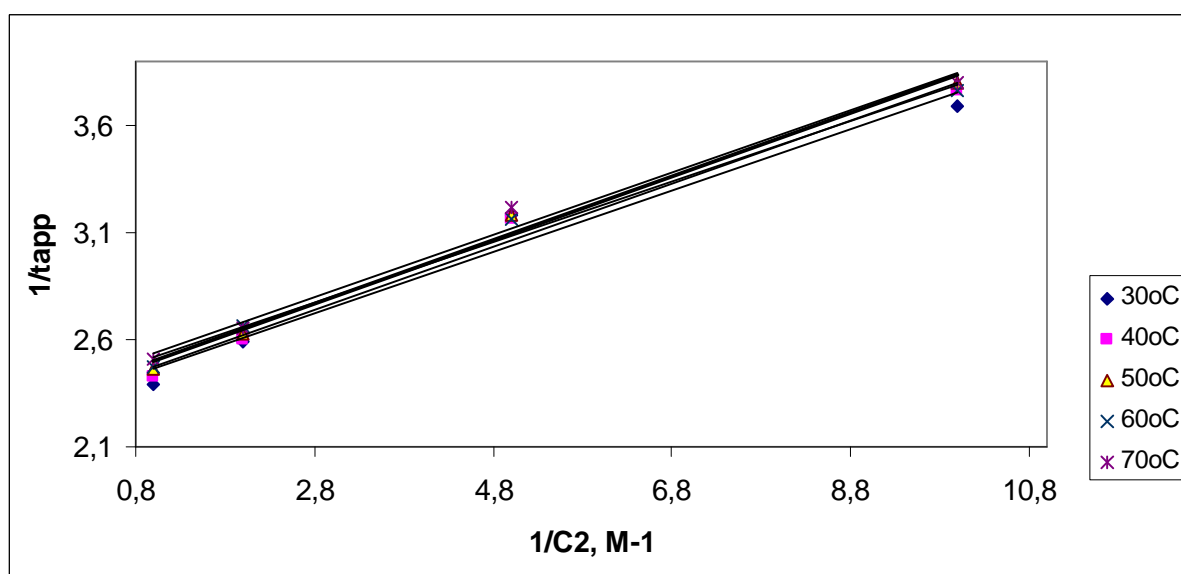


Figure 3  $1/t_{app}$  vs  $1/C_2$  in contact with different electrolytes (at high concentrations)

By means of equation (4) the values of mobility ratio of ions in the membrane phase  $u_+/u_-$ , were calculated.

$$\alpha = \frac{u_+}{u_+ + u_-} \tag{4}$$

Once  $\alpha$  and  $\beta$  values are known, the fixed charge in the membrane at low concentrations  $X_d$  and high concentrations  $X_c$  can be obtained from the slopes of the straight lines represented in Figures 2a, 2b, 2c, 3a, 3b, and 3c. The values of  $\alpha$ ,  $\beta$ , ( $u_+/u_-$ ),  $X_c$ , and  $X_d$  are shown in Tables 2, 3, and 4

Table 2 Values of  $\alpha$ ,  $\beta$ ,  $X_d$ , and  $X_c$  for NaCl electrolyte at different temperatures

(°C)	$\alpha$	$\beta$	(u <sub>+</sub> /u <sub>-</sub> )	$X_d$ (eq. l <sup>-1</sup> )	$X_c$ (eq. l <sup>-1</sup> )
30	0.527	1.421	1.114	0.087	0.022
40	0.534	1.301	1.146	0.088	0.023
50	0.536	1.347	1.155	0.090	0.024
60	0.538	1.370	1.165	0.093	0.025
70	0.540	1.364	1.174	0.095	0.026

Table 3 Values of  $\alpha$ ,  $\beta$ ,  $X_d$ , and  $X_c$  for KCl electrolyte at different temperatures

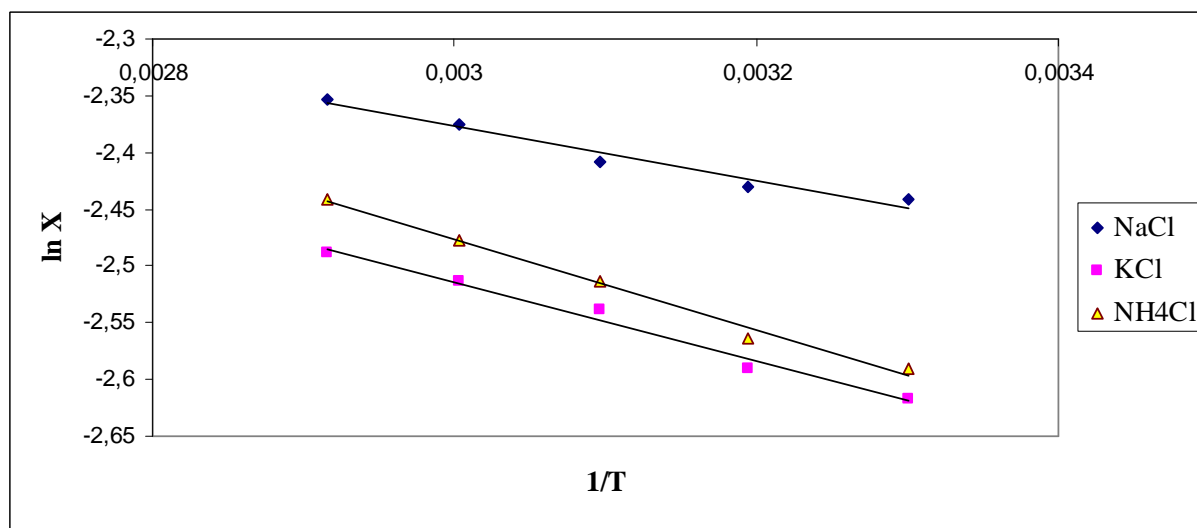
(°C)	$\alpha$	$\beta$	(u <sub>+</sub> /u <sub>-</sub> )	$X_d$ (eq. l <sup>-1</sup> )	$X_c$ (eq. l <sup>-1</sup> )
30	0.580	1.382	1.381	0.073	0.025
40	0.581	1.356	1.387	0.075	0.023
50	0.584	1.396	1.404	0.079	0.021
60	0.590	1.375	1.439	0.081	0.020
70	0.594	1.375	1.463	0.083	0.019

Table 4 Values of  $\alpha$ ,  $\beta$ ,  $X_d$ , and  $X_c$  for NH<sub>4</sub>Cl electrolyte at different temperatures

(°C)	$\alpha$	$\beta$	(u <sub>+</sub> /u <sub>-</sub> )	$X_d$ (eq. l <sup>-1</sup> )	$X_c$ (eq. l <sup>-1</sup> )
30	0.584	1.308	1.404	0.075	0.027
40	0.588	1.304	1.427	0.077	0.025
50	0.593	1.292	1.457	0.081	0.022
60	0.597	1.297	1.481	0.084	0.021
70	0.605	1.264	1.532	0.087	0.018

From Tables 2, 3, and 4, we note that the values of the mobility ratio of the ions in the membrane phase, (u<sub>+</sub>/u<sub>-</sub>), are increased with temperature, it will be seen that for the present study the following order exists: NH<sub>4</sub>Cl > KCl > NaCl. In case of NaCl, mobility ratio values are low and the differences among them are also low. This order may apparently lead to the conclusion that the ion size is the controlling factor; the larger ion diffuses in the membrane phase more slowly than the smaller one and then has low mobility.

The plots of  $\ln X_d$  of various electrolytes against 1/T are shown in Figure 4 from which values of energy of activation  $E_a$  are obtained and are given in Table 5

Figure 4 Plots of  $\ln X$  against  $1/T$  of various electrolytes at different temperatures

The activation thermodynamics parameters, enthalpy of activation  $\Delta H^\ddagger$ , entropy of activation  $\Delta S^\ddagger$  and free energy of activation  $\Delta G^\ddagger$  have been estimated using the alternative form of Arrhenius equation given below



$$\ln X_b = \ln \frac{K_B T}{h} + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \quad (5)$$

Where  $h$  is Planck's constant and  $K_B$  is Boltzmann constant. The plots of  $\ln X_b$  vs.  $1/T$  of various electrolytes at different temperatures for silver thiosulphate membrane extracts gave straight lines as shown in Figure 4. The values of  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  were calculated from the slopes and intercepts, respectively and are listed in Table 5. Where it is found that the activation energy is equal to enthalpy of activation ( $E_a \approx \Delta H^{\ddagger}$ ). The data of present study indicate that electrolyte permeation gives rise to negative values of  $\Delta S^{\ddagger}$  for all the electrolytes used. The negative value of  $\Delta S^{\ddagger}$  indicates electrolyte diffusion with partial immobility increases in a relative manner with increase in valence and hydrated ionic size of the permeating species.

Table 5 Experimental activation energy and other thermodynamic parameters for various electrolytes

Electrolytes	$E_a$ kJ mol <sup>-1</sup>	$\Delta H^{\ddagger}$ kJ mol <sup>-1</sup>	$\Delta S^{\ddagger}$ J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G^{\ddagger}$ kJ mol <sup>-1</sup>
NaCl	1.99	1.99	-259	79
KCl	2.89	2.89	-257	80
NH <sub>4</sub> Cl	3.31	3.32	-255	79

## CONCLUSION

The membrane potentials across parchment supported silver thiosulfate membrane have been measured and found to increase with temperature. The mobility ratio of the ions in the membrane phase are also increased with temperature with the following order: NH<sub>4</sub>Cl > KCl > NaCl. This order may apparently lead to the conclusion that the ion size is the controlling factor. The thermodynamic parameters,  $\Delta H^{\ddagger}$ ,  $\Delta S^{\ddagger}$  and  $\Delta G^{\ddagger}$ , have been estimated using the alternative form of Arrhenius equation. The negative value of  $\Delta S^{\ddagger}$  indicates electrolyte permeation with partial immobilization in the membrane, the partial immobility increases in a relative manner with increase in the valence of the ions constituting the electrolyte.

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## REFERENCES

- [1] Lakshminarayanaiah N., *Chem. Rev.*, **1965**, 65 (5), 491
- [2] Lin Y. S., Burggraaf A. J., *J. Am. Ceram. Soc.*, **1991**, 74, 219
- [3] Siddiqi F. A. et al., *J. Polym. Sci.*, **1971**, 9, 2853
- [4] Siddiqi F. A. et al., *J. Polym. Sci.*, **1971**, 9, 2869
- [5] Siddiqi F. A. et al., *Bull. Chem. Soc. Jpn.*, **1976**, 49 (10), 2858
- [6] Siddiqi F. A. et al., *Bull. Chem. Soc. Jpn.*, **1976**, 49 (10), 2864
- [7] Siddiqi F. A. and Pratap S., *J. Electroanal. Chem.*, **1969**, 23, 137
- [8] Siddiqi F. A., Beg M. N., and Singh S. P., *J. Polym. Sci.*, **1977**, 15, 959
- [9] Siddiqi F. A., Beg M. N., and Prakash P., *J. Electroanal. Chem.*, **1977**, 80, 233
- [10] Badrul Islam and Elhaddad S., *Int. J. Chem. Sci.*, **2012**, 10(2), 1043
- [11] Ansari M. A., et al., *Adv. Appl. Sci. Res.*, **2012**, 3 (1), 251
- [12] Beg M. N. and Matin M. A., *J. Membr. Sci.*, **2002**, 196, 95
- [13] Khan M. M. A., et al. *J. of Ind. Eng. Chem.*, **2012**, 18, 1813
- [14] Khan M. M. A., et al. *J. Ind. Eng. Chem.*, **2012**, 18, 1391
- [15] Kumar, Rakesh, Obrai, Sangeeta, Harmaz, Aparna, *Der. Chem. Sinica*. **2011**, 2(4), 219
- [16] Marathe Yogesh V. and Shrivastava V. S., *Adv. Appl. Sci. Res.*, **2011**, 2(3): 295
- [17] Yadav S. K., Thakur A. N., Kumar A., Singh S. N., Mourya K. C. and Srivastava V. P., *Der. Chem. Sinica*. **2011**, 2(1) 149-156
- [18] Bompilwar S. D., Kondwar S. B., Tabhane V. A., Kargirwar S. R., *Adv. Appl. Sci. Res.* **2010**, 1(1) : 166-173
- [19] Kobatake Y., Noriaki T., Toyoshima Y., and Fujita A., *J. Phys. Chem.*, **1965**, 69, 3981