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Ion-Permeation Rate of (1:1) Electrolytes across Parchment-Supported Silver Chloride Membrane

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Abstract

The ion transport across parchment-supported silver chloride membrane has been investigated. The parchment supported AgCl membrane was prepared by the method of interaction using $AgNO_3$ and NaCl solutions. The transport of different (1:1) electrolytes across parchment-supported silver chloride membrane has been evaluated in terms of the permeation rate which has been determined conductmetrically. The effect of concentration of the electrolyte, kind of ion, and the size of the ion on the permeation rate have been studied. The permeation rate decreases with increasing the concentration of the electrolyte and the size of the ion. However, the influence of the cation is larger than the anion indicating that the membrane is cation selective. The permeation rates before and after the treatment of the parchment paper with AgCl has been compared. The ion selectivity of the parchment paper has been strongly enhanced after the treatment

Keywords: Ion permeation, parchment-supported membrane

Contents

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1. Introduction

The developments of various membranes have gained much attention during last three decades, on account of their utilization for the economic separation processes. In this regard ion-exchange membranes have emerged as the most advance and economical separation membranes. These membranes are being widely used for the processes like electro dialysis of sea water or brackish water, separation of inorganic toxic metal ions, pharmaceutical products, sugar processing and beverages industries[1-12]. Inorganic precipitate membranes because of their stability in various environmental situations have quite often been utilized as a model for the studies of transport phenomena. A series of papers[13-23] have reported the preparation of various types of membranes using inorganic precipitates and supports/binders and have utilized them as model to study the mechanism of transport of ions as well as to test the validity of some recently developed equations for membrane potential.

In this work, we describe the preparation of silver chloride parchment-supported membrane and using the conductometric measurements to determine the permeation rate of different (1:1) electrolytes

2. Materials and Methods

All the reagents used were of AR grade and their solutions were prepared in de-ionized water. The electrolytes examined were lithium chloride, sodium chloride, potassium chloride, ammonium chloride, sodium bromide, sodium iodide, sodium nitrate, and sodium nitrite. All of these electrolytes were monovalent (1:1).

2.1 Preparation of Membrane

The parchment-supported silver chloride membrane was prepared by the method of interaction described by Siddiqi et al[24,25]. The parchment paper was tied carefully between the two compartments of the measuring cell (Figure 1) in which a solution of 0.2 M silver nitrate in one side and a solution of 0.2 M sodium chloride in the other side were added and left for 72 hrs. The two solutions were interchanged later and kept for another 72 hrs. The membrane thus prepared was thoroughly washed with de-ionized water for removal of free electrolyte.

2.2 Determination of Molar conductivity Λ_m

In order to determine the molar conductivity for each electrolyte, the conductivity of different electrolyte concentrations in very dilute range (4×10^{-6}, 8×10^{-6}, 1.2×10^{-5}, 1.6×10^{-5}, and 2×10^{-5} M) using Conductometer 703 from Knick Company were measured. The conductivity values were then plotted against the concentrations. The slope of the relationship is equal to the molar conductivity for the electrolyte. The values of molar conductivity are shown in Table 1.

Table 1. The molar conductivity (Λ_m) of examined electrolytes

Λ_m mS cm^2 mol^{-1}	Electrolyte
96545	NaCl
105000	KCl
81091	LiCl
104727	NH_4Cl
98864	NaBr
97409	NaI
88864	$NaNO_2$
87209	$NaNO_3$

2.3 Permeation rate determination

In order to study the ion permeation across treated and untreated parchment paper, the home-made U-shaped cell shown in Figure 1 was used. The cell consists of two chambers separated by the membrane with the cross section area A being 6.47 cm^2. One of the chambers contains a certain volume (V_0= 75 ml) of the aqueous salt solution (concentration = 0.1 M for the study of the type of ion and different concentrations for the study the effect of the concentration) and the other one is filled with the same volume of de-ionized water. The initial increase in conductivity ($\Delta\Lambda/\Delta t$) in the water chamber was measured using a Conductometer 703 from Knick Company.

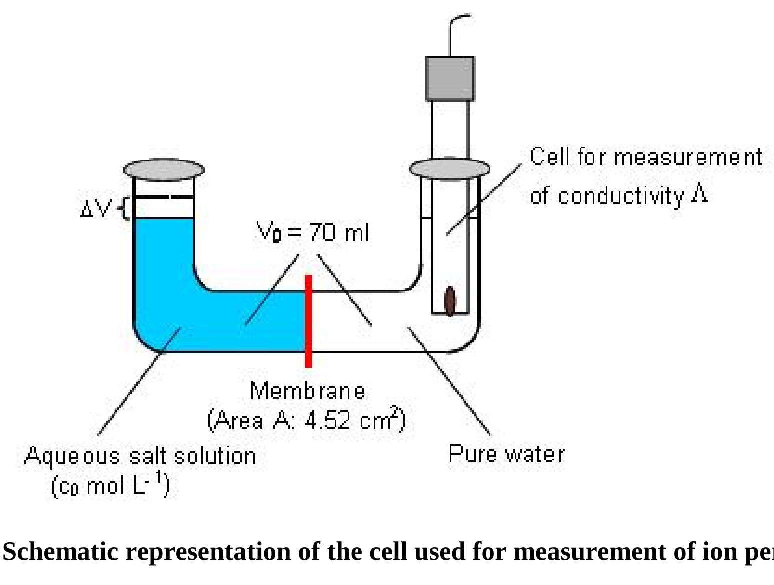

Figure 1. Schematic representation of the cell used for measurement of ion permeation

The permeation rate P_R (cm s^{-1}) was calculated using equation1 shown below:

$$P_R = \left(\frac{\Delta\Lambda}{\Delta t}\right)(V_0 - \Delta V)\Lambda_m^{-1}(Ac_0)^{-1},^{5} \quad (1)$$

Where: Λ_m is the molar conductivity, and ΔV is the change of the volume after permeation. Permeation rates displayed are always the average values of two permeation measurements across the same membrane.

3. Results and Discussion

The permeation rates for series of 1:1 monovalent electrolytes across the parchment paper before and after treatment with silver chloride precipitate have been studied and compared. The permeation rates have been studied in terms of:
1. The effect of concentration
2. The effect of charge and size of ion

To determine the permeation, firstly the increase in conductivity with time (each 5 min) in water chamber (Figure 1) was measured using a Conductometer 703 from Knick Company. The values of conductivity were then plotted against time. The slope of the curve (ΔΛ/Δt) was determined and the equation 1 was used to determine the permeation rate of each electrolyte across the membrane.

3.1 The effect of concentration on permeation rate

Different concentration [0.001 M, 0.005 M, 0.01 M, 0.05 M, and 0.1 M] of sodium chloride solutions have been used to study the effect of the concentration on the permeation rate. The permeations of different concentrations before and after the treatment have been compared.

The conductivity values after each 5 min before and after treatment have been measured and plotted against time and shown in Figure 2 and 3. The slope of the linear curve was used to calculate the permeation rate of the electrolyte. The values of permeation rate are shown in Table 2 and also compared before and after the treatment in Figure 4

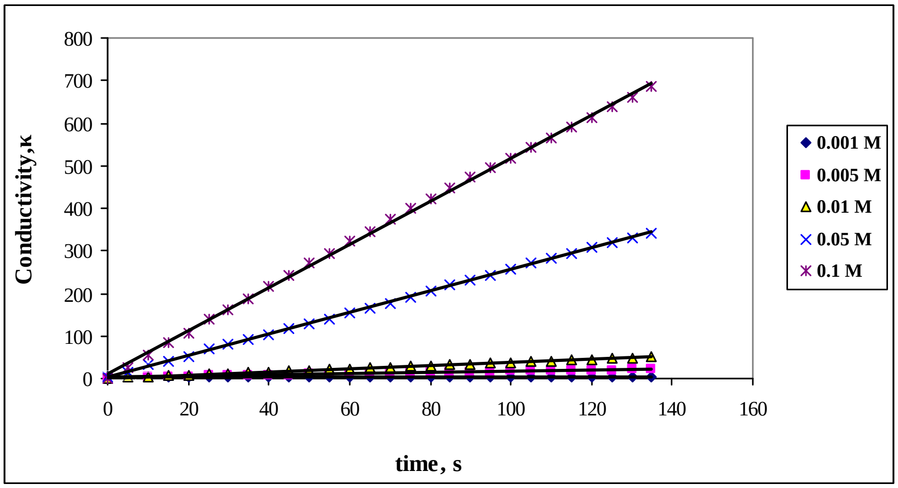

Figure 2. Conductivity VS Time for different concentration of NaCl before treatment

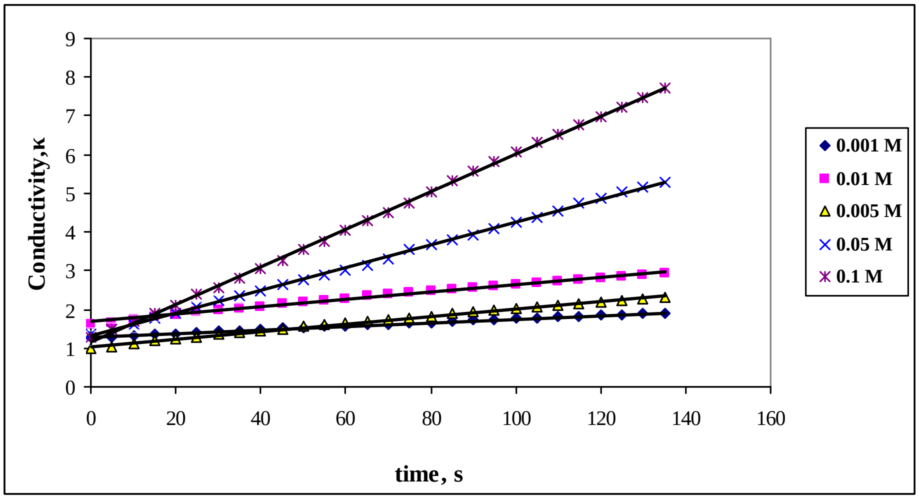

Figure 3. Conductivity VS Time for different concentration of NaCl after treatment

Table 2. Values of Permeation Rate for different concentration of NaCl before and after treatment

Concentration M	Before Treatment ($cm\ s^{-1}$) N X 10^{-4}	After Treatment ($cm\ s^{-1}$) N X 10^{-4}
0.001	0.350	0.0921
0.005	0.564	0.0384
0.01	0.724	0.0192
0.05	1.010	0.0118
0.1	1.020	0.0097

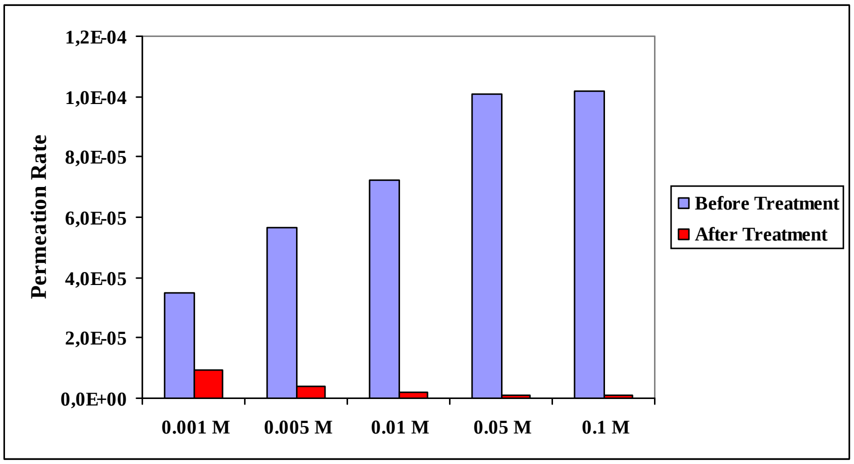

Figure 4. Permeation rate for different concentration of NaCl before and after treatment

The permeation rate increases with concentration before treatment because the concentration is the controlling factor of electrolyte diffusion. However, the situation is changed after the treatment; the permeation decreases with concentration. This can be attributed to the presence of charged fixed group on the membrane after the treatment which came as a result of the ability of silver chloride precipitate of adsorption of ions from the electrolyte solution. As the concentration increases the adsorption also increases which will decrease the permeation of the electrolyte solution across the membrane. Generally, there was a significant decrease in the permeation of different concentrations of sodium chloride in the presence of silver chloride membrane which ranges before and after treatment between 4-times (0.001 M) to 105-times (0.1 M).

3.2 The effect of charge of ions on permeation rate

3.2.1 Permeation of electrolytes with different monovalent cations

Different electrolytes solutions with same anion (chloride ion) and different monovalent cations [LiCl, NaCl, KCl, and NH_4Cl] have been used to study the effect of charge on the permeation rate. The permeations of these electrolytes before and after the treatment have been compared.

The conductivity values after each 5 min before and after treatment have been measured and plotted against time and shown in Figure 5 and 6. The slope of the linear curve was used to calculate the permeation rate of the electrolyte. The values of permeation rate are shown in Table 3 and also compared before and after the treatment in Figure 7.

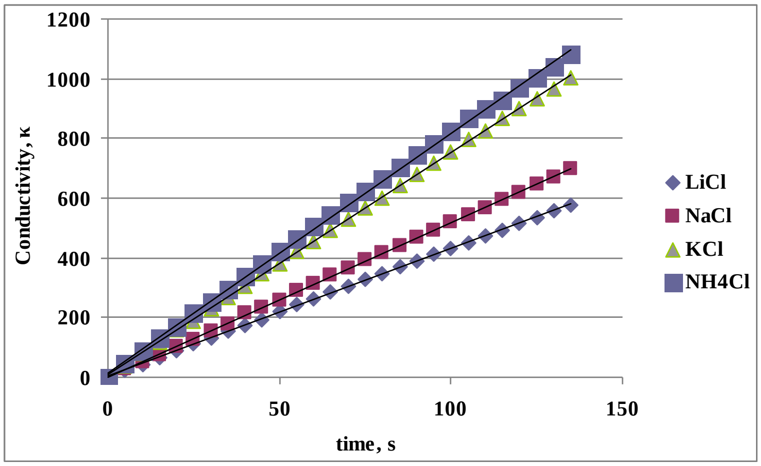

Figure 5. Conductivity VS Time for different electrolytes before treatment

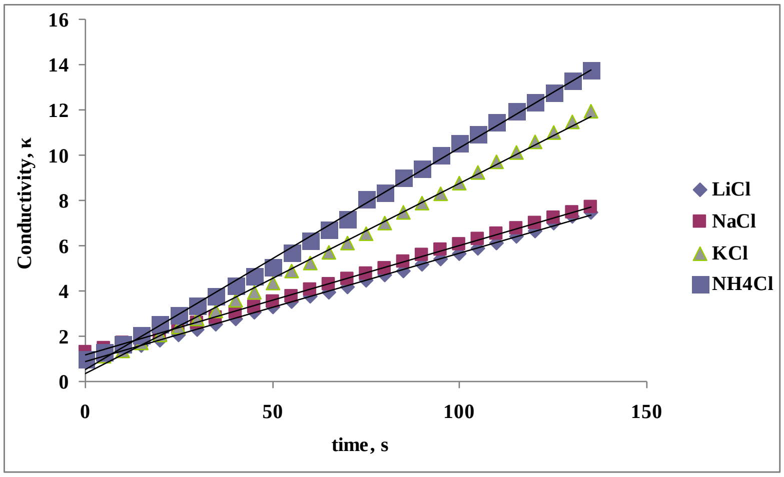

Figure 6. Conductivity VS Time for different electrolytes after treatment

Table 3. Values of Permeation Rate for different electrolytes of same anion before and after treatment

Electrolyte	Before Treatment (cm s^{-1}) N X 10^{-4}	After Treatment (cm s^{-1}) N X 10^{-4}
LiCl	1.020	0.0115
NaCl	1.040	0.0097
KCl	1.370	0.0155
NH_4Cl	1.480	0.0181

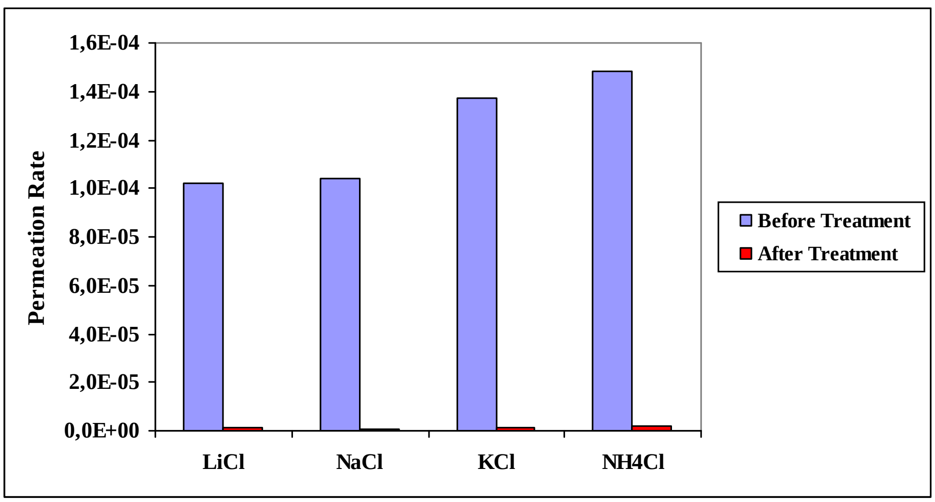

Figure 7. Permeation rate for different electrolytes of same anion before and after treatment

The permeation rate increases as the size of cation decreases (Li > Na > K ~ NH_4) before indicating that the controlling factor is the pore size of the membrane. However, the pores became tighter after the treatment and the membrane had a fixed charge; therefore the permeation rate decreased more dramatically compared with before the treatment. The difference in permeation rate between LiCl and NaCl after the treatment decreased because there are two opposite factors controlling the permeation across the membrane; the pore size and the charge density on the membrane. However, no clear differences in the permeations of different cations because the cations were all monovalent. Generally, there was a significant decrease in the permeation of these electrolytes in the presence of silver chloride membrane which were as follows: 89-times for LiCl, 110-times for NaCl, 89-times for KCl, and 81-times for NH_4Cl.

3.2.2 Permeation of electrolytes with different monovalent anions

Different electrolytes solutions with same cation (sodium ion) and different monovalent anions [NaCl, NaBr, NaI, $NaNO_2$, and $NaNO_3$] have been used to study the effect of charge on the permeation rate. The permeations of these electrolytes before and after the treatment have been compared.

The conductivity values after each 5 min before and after treatment have been measured and plotted against time and shown in Figure 8 and 9. The slope of the linear curve was used to calculate the permeation rate of the electrolyte. The values of permeation rate are shown in Table 4 and also compared before and after the treatment in Figure 10.

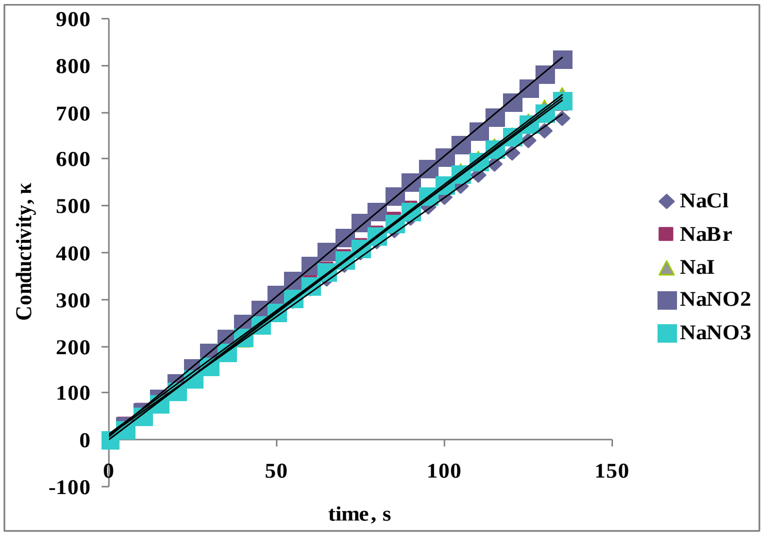

Figure 8. Conductivity VS Time for different electrolytes before treatment

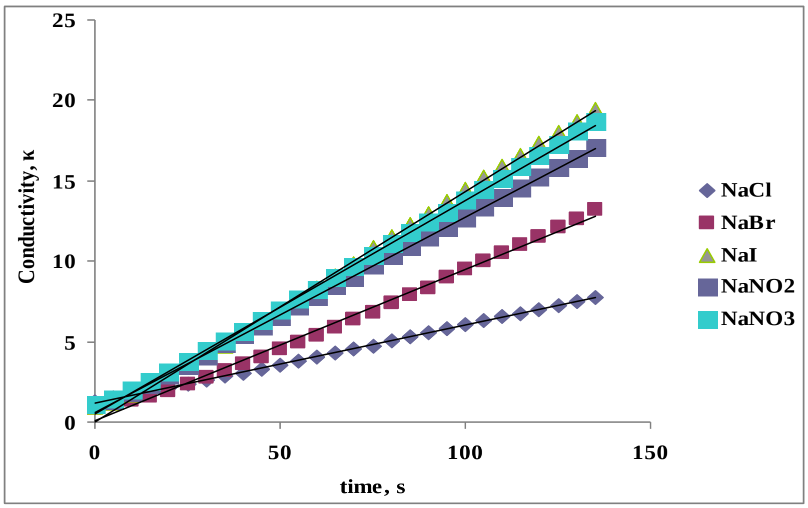

Figure 9. Conductivity VS Time for different electrolytes after treatment

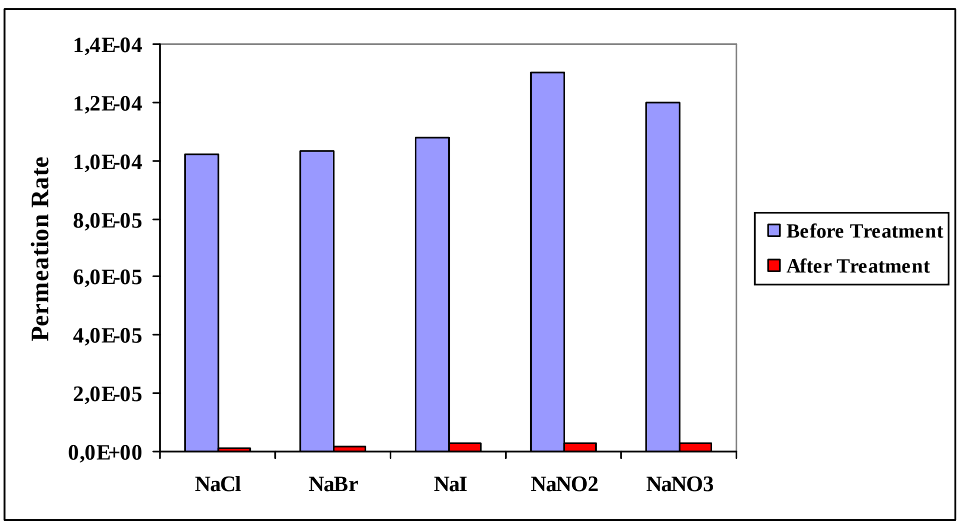

Figure 10. Permeation rate for different electrolytes of same cation before and after treatment

Table 4. Values of Permeation Rate for different electrolytes before and after treatment

Electrolyte	Before Treatment (cm s^{-1}) N X 10^{-4}	After Treatment (cm s^{-1}) N X 10^{-4}
NaCl	1.02	0.0097
NaBr	1.030	0.0184
NaI	1.08	0.0284
$NaNO_2$	1.30	0.0264
$NaNO_3$	1.20	0.0295

There were not differences in permeation rates of these electrolytes before treatment because there are no such differences in the size of the examined anions (Cl^-, Br^-, I^-, NO_2^-, and NO_3^-). However, after the treatment were some differences in the permeations ($NaNO_3$ > NaI > $NaNO_2$ > NaBr > NaCl) which can be attributed to two factors: the pore size which became tighter and the fixed charge groups on the membrane. The halide ions (especially; Cl^- and Br^-) are more adsorbed than the other anions and therefore the membrane becomes more selective for excluding the anions which lower the permeation rate. The fixed charge also becomes more effective to exclude the ions as the pore size decreases. Generally, there was a significant decrease in the permeation of these electrolytes in the presence of silver chloride membrane which were as follows: 105-times for NaCl, 56-times for NaBr, 38-times for NaI, 49-times for $NaNO_2$, and 41-times for $NaNO_3$.

The permeation rates of different electrolytes after the treatment were compared in Figure 11

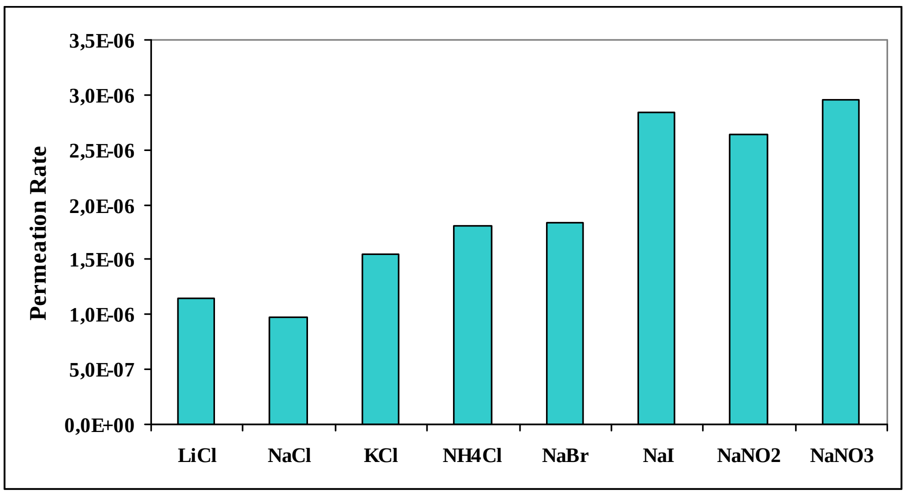

Figure 11. Comparison of permeation rate for different electrolytes after treatment

NaCl had the lowest permeation and $NaNO_3$ and NaI had the fastest one [the permeation of $NaNO_3$ and NaI is 3-times the permeation of NaCl].

4. Conclusion

Three factors controlling the permeation across the parchment-supported silver chloride membrane. These factors are: the concentration, the pore size, and the fixed charge groups which can be attributed to the adsorption of ions from the examined solution. The treatment of the parchment paper with AgCl decreases the pore size and therefore the permeation. The presence of the inorganic precipitate on the parchment paper results in adsorption of anions from the electrolyte solution which depends on the concentration of the electrolyte and the type of anions. As the concentration increases the adsorption also increases which results in increasing the charge density on the membrane and therefore the permeation will decrease. Some anions adsorb more than others (especially chloride ion in the present study) which therefore increase the charge density and as a consequence the permeation of the electrolyte will decrease.

5. References

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