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ORIGINAL ARTICLE

Reduced Transport Numbers of PolysulfoneMembranes From The Initial Time EMF Measurements

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ABSTRACT

Initial membrane potentials of polysulfone cation exchange membranes were measured with KCl, NaCl, LiCl $CaCl_2$ and $FeCl_3$ solutions by using Ag/AgCl electrodes. The measurements were carried out for KCl / unsupported polysulfone cation exchange membranes (SA_3S) or polyester supported polysulfone cation exchange membranes (SA_3T) / KCl, NaCI, LiCI, $CaCl_2$ and $FeCl_3$ systems. The concentration of KCl, C_1, was kept constant at 1.10^{-2} M in one cell; however the concentrations of KCl, NaCI, LiCl, $CaCl_2$ and $FeCl_3$, $C_{2,}$ in the other cell were changed from 1.10^{-4} M to 2.0 M. The Supported face of SA_3T membrane was brought to equilubrium with the left- hand solution and then, the unsupported face of SA_3T membrane was exposed to the right-hand solution. Transport number of K^+, Na^+, Li^+, Ca^{+2}, Fe^{+3} ions corresponding to the each of two surface layers of the membrane was evaluated from the initial time and the fifth minute emf measurements. The results were compared with between unsupported polysulfone cation exchange membranes and polyester supported polysulfone cation exchange membranes

Keywords: The mean reduced transport number, τ_{mean}; Initial time; Cation exchange membrane

Article Outline

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1. INTRODUCTION

The description of transport phenomena in unsupported polysulfone cation exchange membranes (SA_3S) and polyester supported polysulfone cation exchange membranes (SA_3T) is still unclear from the physical chemistry viewpoint. The outer and inner surface of SA_3T membranes are different. The inner surface is more homogeneous with its abundance of charged group. On the other hand, the outer surface appears a more heterogeneous. Asymmetric behaviors in SA_3T membranes were firstly pointed out by Yamada et al [1].

The asymmetry potentials of heterogeneous membrane were studied [2,3] when the membranes were in contact with identical electrolyte solution on both side. As expected, the asymmetry potentials of SA_3T can be varied with time and vanish eventually. The asymmetry of ion exchange membranes are studied electrochemically by initial time and fifth minute electromotive force (EMF) measurements in well stirred concentration cell and by reversing the orientation of the membrane. Generally, the interpretation about emf from such experiments is complex, because the emf is complicated function of the salt concentration profile in the membrane with asymmetry in the fixed charge distribution. The initial time emf method was first developed and investigated by Compan et al. [4,5,6,7] who applied to the electrochemical method to asymmetric polysulfone cellulose acetate phenol-sulphonic acid membrane and polysulfone ultra filtration membranes. They investigated the initial time experiments on asymmetric having polyester support layer using small concentration differences.

In this study, the transport numbers for K^+, Na^+, Li^+, Ca^{+2}, Fe^{+3} in the surface layers of SA_3S and SA_3T membranes were evaluated from initial time and fifth minute measurements at each face of the membranes.

The EMF values of initial time and fifth minute may predict the inter facial asymmetry by means of the concentration dependence of the transport numbers for membrane surfaces. In this study, the asymmetry of the two surfaces of the SA_3T membranes was investigated by use of initial time EMF method as well as fifth minute emf method. Results were compared with SA_3S membranes. The aim of this study is to show that emf values might be used to indicate the presence of asymmetry in the SA_3T membranes.

2. EXPERIMENTAL

2.1. Materials

The chemicals used in whole experiments from Merck were obtained and were used without further purification. The cation exchange membranes, polysulfone (SA_3S homogeneous) and polysulfone with polyester support (SA_3T heterogeneous) from Gellman Science were used. The basic properties of both membranes are; ion exchange capaties 1.522 and 1.132 meg.g^{-1} for SA_3S and SA_3T, respectively, pore size is 0.45 μm and thickness is 152.4 μm.The cation exchange membranes were supplied in hydrogen form. All of the experiment was carried out at 25 ^oC.

2.2. Initial Time and Fifth Minute Membrane Potentials

First of all the samples of membranes were pretreated by boiling for 60-70 min. in deionized water. After that this samples were treated with 1.0 M HNO_3, 1.0M NaOH and water respectivelly. Finally these were put in 0.01M HCl to obtain the H^+ ions during 24h. Before the experiments, SA_3S and SA_3T membranes were conditioned with 0.01 M KCl solution. Equilibrated membranes were put in a cell with two chambers whose volumes are 50 ml. The effective membrane area was 7.07 cm^2. The concentration of KCl, $C_{1,}$ was kept constant at 1.0 x 10^{-2} M in one cell, however the concentrations of KCl, NaCI, LiCl, $CaCl_2$ and $FeCl_3$ in other cell, C_2, was changed from 1.0 x 10^{-4} M to 2.0 M.The Supported face of SA_3T membrane was brought to equilibrium with the left- hand solution and then, the unsupported face of SA_3T membrane was exposed to the right-hand solution. The initial time emf values and fifth minute EMF values were measured by means of DC Meter (nA Range 200 function mV) with Ag / AgCl electrodes. The experiments were also performed by changing both sides of supported membrane (SA_3T) in order to determine its characteristic properties. It was expected that SA_3T gives different potential properties due to its heterogeneity.

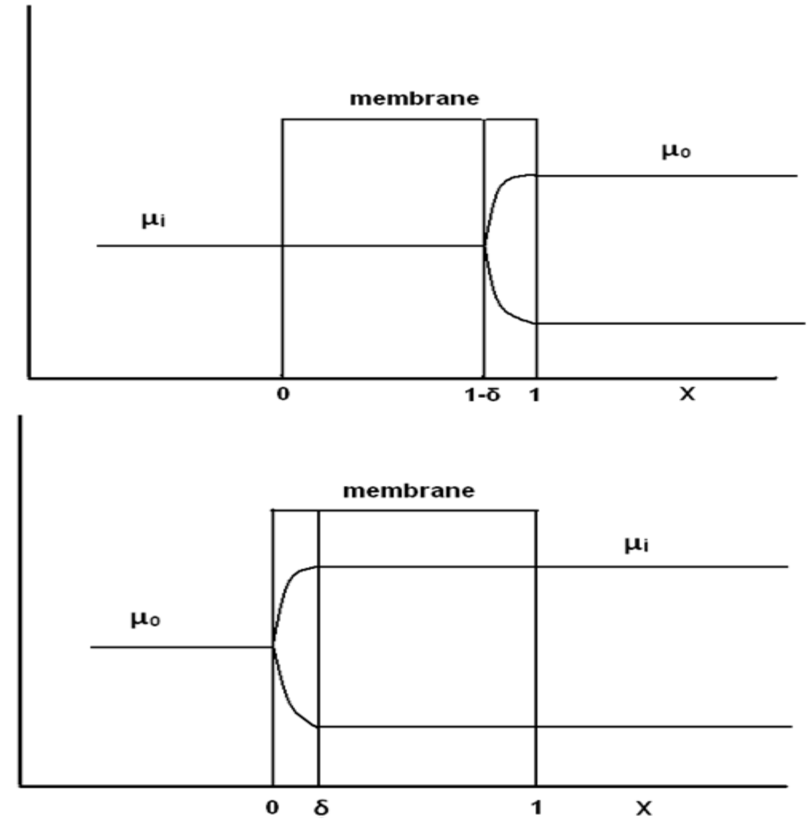


Figure 1. Salt chemical potential profiles in the membrane corresponding to initial time EMF characterization of the right and the left hand face of the membrane.

Fig.1. shows the concentration profile when the diffusion process starts. The upper picture corresponds to measurements of the EMF at the right hand side and the lower one to measurements of the EMF at the left hand side [6].

When we are doing initial time measurements we can consider the transport number as a constant in an interval δ because the concentration, as we have shown in Fig. 1, varies only in a thin layer inside the membrane.

$$EMF_{right} = -\frac{RT}{F}\,\tau_2(right)\,ln\left(\frac{a_R}{a_L}\right) \quad (1)$$

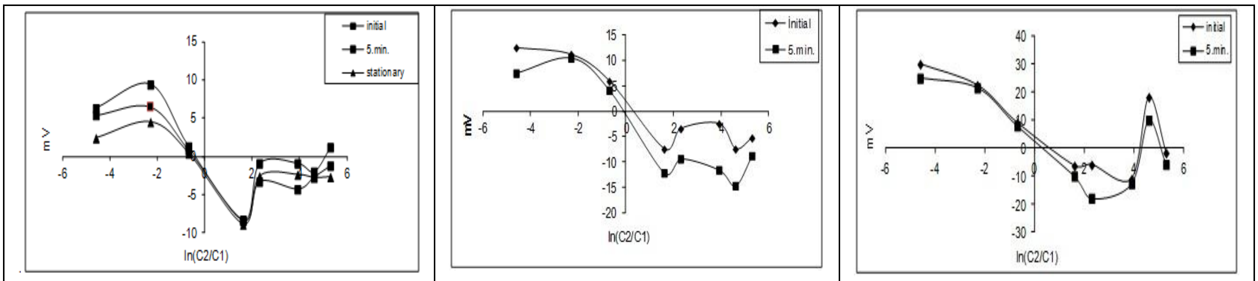
$$EMF_{left} = -\frac{RT}{F}\,\tau_2(left)\,ln\left(\frac{a_R}{a_L}\right) \quad (2)$$

These expressions permit a characterization of each of the surface layers of the membrane and make possible a determination of the two reduced transport numbers corresponding to the near interfacial layers of an asymmetric membrane. The asymmetry is given by the difference between the surface layer transport numbers. The 'initial' EMF values have all been taken after 15 s of contact of the membrane face with the new solution. The 'mean reduced transport numbers' under stationary state conditions are calculated by formulas similar to Eqs. (1) and (2) for the two orientations of the membrane. The stationary EMF values were read after the observation of a constant voltage during one half hour, controlling also that the conductivities in the electrode chambers did not change during the measurements.

Stirring, which is most important for the stationary state EMF measurements [6], were performed in each electrode chamber by means of high rpm magnetic stirrers. The rotation speed was taken as high as possible, and no changes in the EMF values could be seen when the rpm was lowered a little.

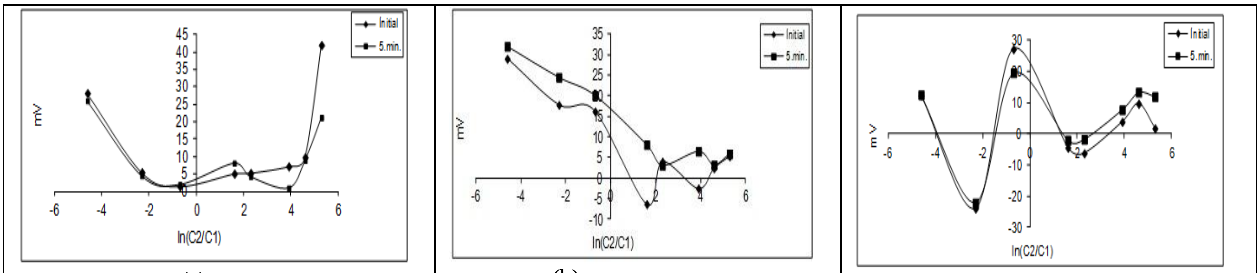
3. RESULTS AND DISCUSSION

In figures 2-6 the graphs of the experimental values at the initial time and the fifth minute versus In(C_2/C_1) at different values of concentration were drawn. Then, R^2 values were calculated from this graps. These values were shown in Table1. Experimental EMF values which were obtained for the membranes with the logarithm of the activity gradients were given remarkably good correlation except for LiCl in SA_3T (supported 0.01 M KCl side), NaCl (supported variation side) and $CaCl_2$ in SA_3T (supported 0.01 M KCl side).



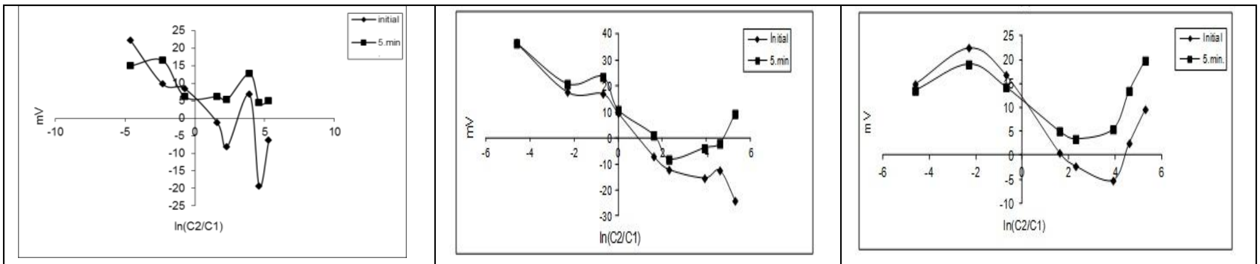
(a) (b) (c)

Figure 2. a. Membrane Potential values of KCl in SA_3S membrane. b. Membrane Potential values of KCl in SA_3T membrane (supported C_1). c. Membrane Potential values of KCl in SA_3T membrane (supported C_2).



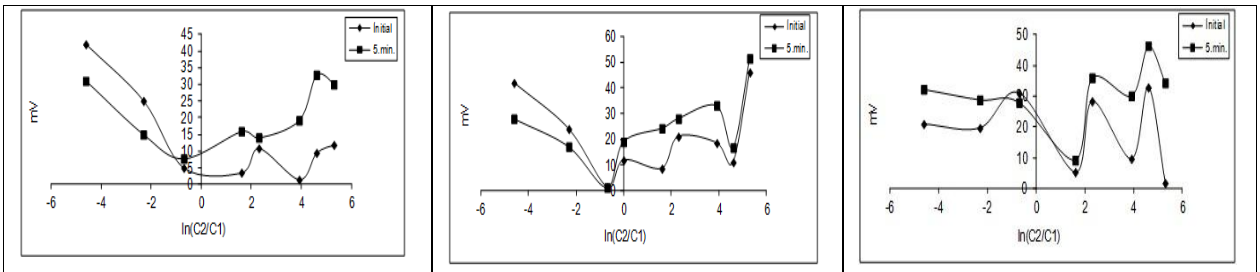
(a) (b) (c)

Figure 3. a. Membrane Potential values of NaCl in SA_3S membrane b. Membrane Potential values of NaCl in SA_3T membrane (supported C_1). c. Membrane Potential values of NaCl in SA_3T membrane (supported C_2).



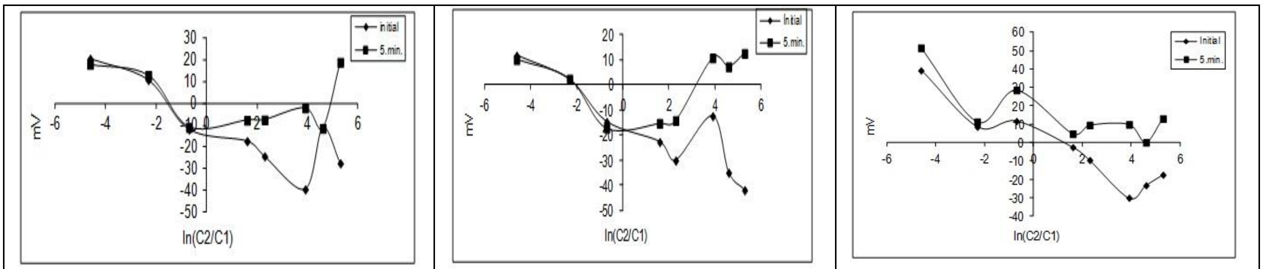
(a) (b) (c)

Figure 4. a. Membrane Potential values of LiCl in SA_3S membrane. b. Membrane Potential values of LiCl in SA_3T membrane (supported C_2). c. Membrane Potential values of LiCl in SA_3T membrane (supported C_1).



(a) (b) (c)

Figure 5. a. Membrane Potential values of $CaCl_2$ in SA_3S membrane. b. Membrane Potential values of $CaCl_2$ in SA_3T membrane (supported C_2). c. Membrane Potential values of $CaCl_2$ in SA_3T membrane (supported C_1).



(a) (b) (c)

Figure 6. a. Membrane Potential values of $FeCl_3$ in SA_3S membrane. b. Membrane Potential values of $FeCl_3$ in SA_3T membrane (supported C_1). c. Membrane Potential values of $FeCl_3$ in SA_3T membrane (supported C_2).

In SA_3T the initial time EMF values at both sides of the membrane must have been equal to zero, but they weren't because of the heterogeneity properties of the membranes. When C_1 is kept constant and C_2 is varied, the slopes of the regression lines are statistically indistinguishable. This means that the apparent transport number of K^+, Na^+, Li^+, Ca^{+2} and Fe^{+3} ions are equal to each other for both faces. This is due to the large concentration differences between both sides. It has been reported that thin layers of the SA_3S and SA_3T membranes vary by depending of their surface layers [8,9,10] as well as either lower or upper concentration changes.

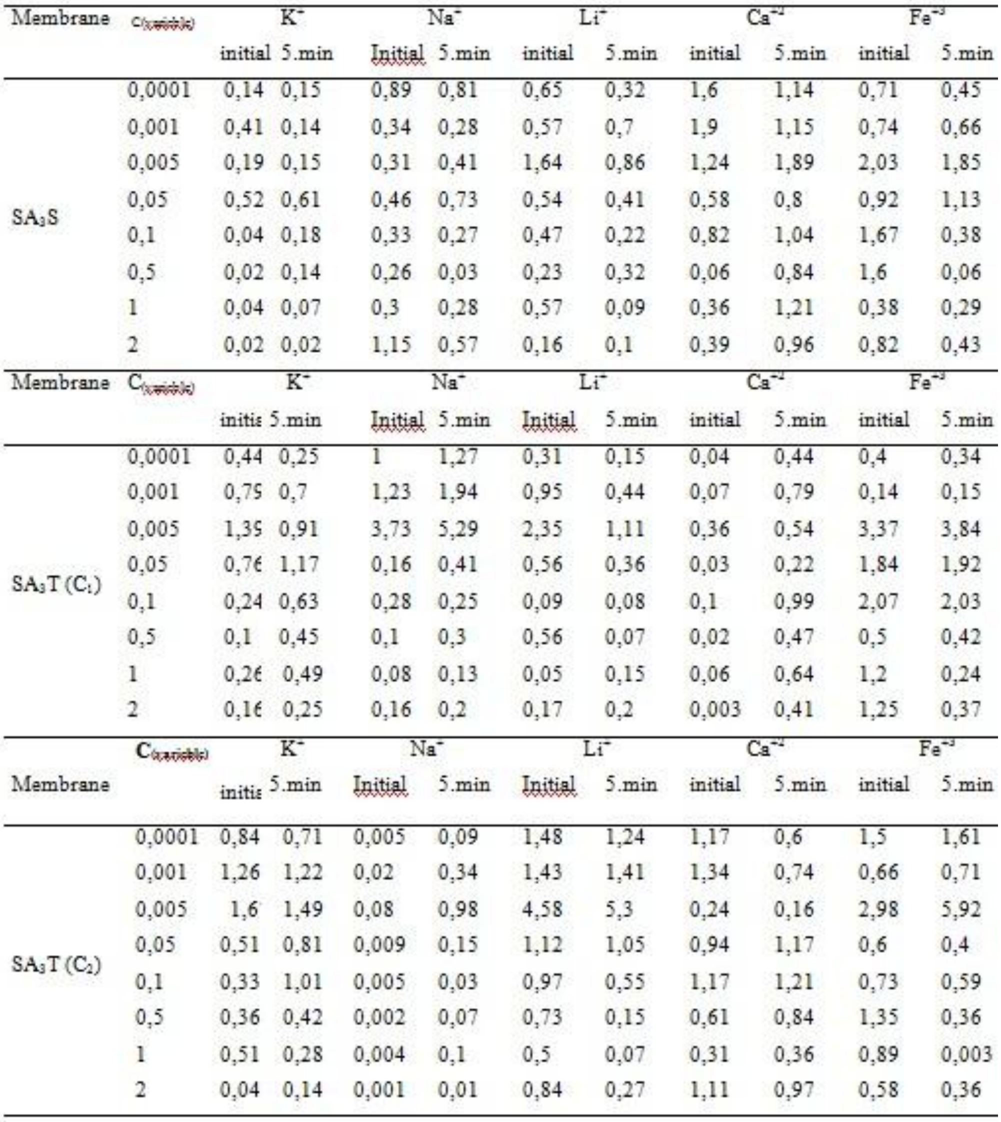
Table 1. R^2 values for the studied membranes under initial and stationary conditions.

	KCl		NaCl		LiCl		$CaCl_2$		$FeCl_3$	
Membrane	initial	5.min	initial	5.min	initial	5.min	initial	5.min	initial	5.min
SA_3S	0,526	0,661	0,748	0,738	0,696	0,506	0,902	0,875	0,812	0,597
$SA_3T\ C_1$	0,844	0,794	0,819	0,937	0,498	0,279	0,041	0,324	0,803	0,795
$SA_3T\ C_2$	0,663	0,674	0,011	0,179	0,953	0,804	0,661	0,511	0,906	0,739

The asymmetric behaviors of the SA_3S and SA_3T membranes were seen very clearly from the experiments data performed with KCl, NaCl, LiCl, $CaCl_2$ and $FeCl_3$ solutions. When compared, the EMF values for two faces of SA_3S and SA_3T membranes were quite close to each other. The highest values were obtained when the concentration differences a crossing the membrane were large. It was point out that membrane potentials obtained in this way give information about the electro kinetic behaviors at the other SA_3T and SA_3T (supported C_2) membrane surface, and on the other hand the membrane potential at lower concentrations are fundamentally Donnan potentials [11,12] It was also noticed that Donan effect is more significant at the inner surface region of the SA_3S and SA_3T membranes. A comparison of the EMF values for asymmetric polysulfone with polyester support membrane seems to be close to the values obtained for SA_3S membrane. We have fitted the EMF vs. $ln\ (a_{variable}/a_{fix})$ data to least square 3rd degree polynomials passing through (0,0) in all four cases (initial left, initial right, stationary in one direction, stationary in the other direction). For the initial time EMF values, the third degree polynomial has been used for easy calculation of the derivative δ (EMF) / δ $\ln a_{variable}$ needed to calculate the surface transport number for each variable concentration. In the case of the stationary state measurements, we define a 'reduced mean transport number' by the relation. There is not much sense in defining the mean value in the differential way analogous to the initial time value, since the stationary EMF is a functional of the whole concentration profile. The mean reduced transport number, τ_{mean}, was calculated by using Eq.(3) [13] and it is shown in.

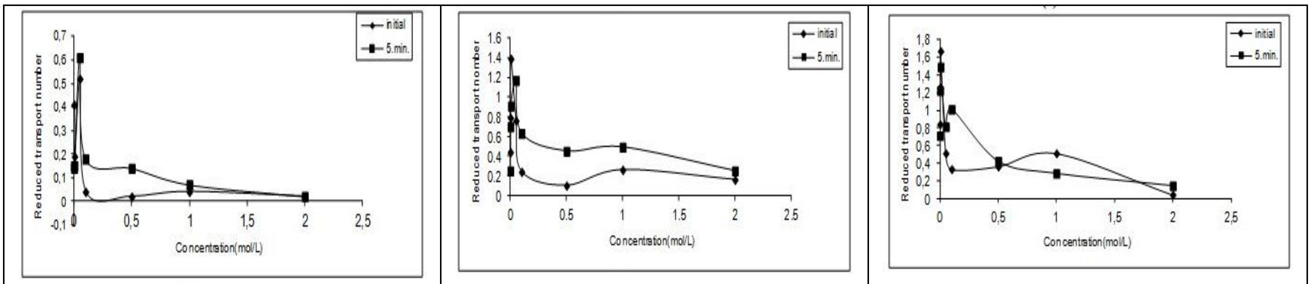
$$\tau_{mean} \equiv (F/2RT)\, x \left| EMF \times (polinomial) \right| \ln (a_{variable}/a_{fix}) \qquad (3)$$

Table 2. τ_{mean} values for the studied membranes under initial and stationary conditions.



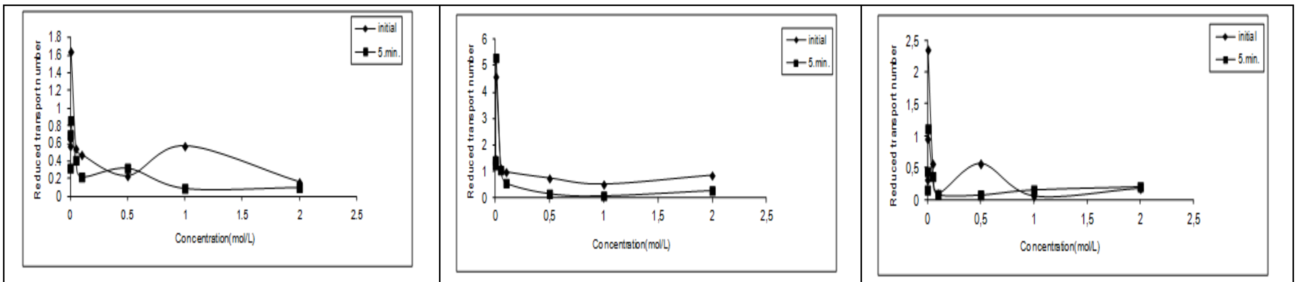
Membrane	$C_{(variable)}$	K^+		Na^+		Li^+		Ca^{+2}		Fe^{+3}	
		initial	5.min	Initial	5.min	initial	5.min	initial	5.min	initial	5.min
SA_3S	0,0001	0,14	0,15	0,89	0,81	0,65	0,32	1,6	1,14	0,71	0,45
	0,001	0,41	0,14	0,34	0,28	0,57	0,7	1,9	1,15	0,74	0,66
	0,005	0,19	0,15	0,31	0,41	1,64	0,86	1,24	1,89	2,03	1,85
	0,05	0,52	0,61	0,46	0,73	0,54	0,41	0,58	0,8	0,92	1,13
	0,1	0,04	0,18	0,33	0,27	0,47	0,22	0,82	1,04	1,67	0,38
	0,5	0,02	0,14	0,26	0,03	0,23	0,32	0,06	0,84	1,6	0,06
	1	0,04	0,07	0,3	0,28	0,57	0,09	0,36	1,21	0,38	0,29
	2	0,02	0,02	1,15	0,57	0,16	0,1	0,39	0,96	0,82	0,43
Membrane	$C_{(variable)}$	K^+		Na^+		Li^+		Ca^{+2}		Fe^{+3}	
		initia	5.min	Initial	5.min	Initial	5.min	initial	5.min	initial	5.min
$SA_3T\ (C_1)$	0,0001	0,44	0,25	1	1,27	0,31	0,15	0,04	0,44	0,4	0,34
	0,001	0,79	0,7	1,23	1,94	0,95	0,44	0,07	0,79	0,14	0,15
	0,005	1,39	0,91	3,73	5,29	2,35	1,11	0,36	0,54	3,37	3,84
	0,05	0,76	1,17	0,16	0,41	0,56	0,36	0,03	0,22	1,84	1,92
	0,1	0,24	0,63	0,28	0,25	0,09	0,08	0,1	0,99	2,07	2,03
	0,5	0,1	0,45	0,1	0,3	0,56	0,07	0,02	0,47	0,5	0,42
	1	0,26	0,49	0,08	0,13	0,05	0,15	0,06	0,64	1,2	0,24
	2	0,16	0,25	0,16	0,2	0,17	0,2	0,003	0,41	1,25	0,37
	$C_{(variable)}$	K^+		Na^+		Li^+		Ca^{+2}		Fe^{+3}	
Membrane		initia	5.min	Initial	5.min	Initial	5.min	initial	5.min	initial	5.min
$SA_3T\ (C_2)$	0,0001	0,84	0,71	0,005	0,09	1,48	1,24	1,17	0,6	1,5	1,61
	0,001	1,26	1,22	0,02	0,34	1,43	1,41	1,34	0,74	0,66	0,71
	0,005	1,6	1,49	0,08	0,98	4,58	5,3	0,24	0,16	2,98	5,92
	0,05	0,51	0,81	0,009	0,15	1,12	1,05	0,94	1,17	0,6	0,4
	0,1	0,33	1,01	0,005	0,03	0,97	0,55	1,17	1,21	0,73	0,59
	0,5	0,36	0,42	0,002	0,07	0,73	0,15	0,61	0,84	1,35	0,36
	1	0,51	0,28	0,004	0,1	0,5	0,07	0,31	0,36	0,89	0,003
	2	0,04	0,14	0,001	0,01	0,84	0,27	1,11	0,97	0,58	0,36

The calculated transport numbers of K^+, Na^+, Li^+, Ca^{+2}, Fe^{+3} ions from initial time and the fifth minute emf measurements in the membranes are plotted as a function of the logarithm of the salt concentration (on logarithmic scale) in Fig. 7-15. It can be seen that the variation of the transport numbers with concentration for both surfaces are very close to each other. The concentration dependence shows differences which are remarkably high at the lower concentration than 0,005M. The graphs for two directions of diffusion are quite close to each other and show similar variations with concentration.



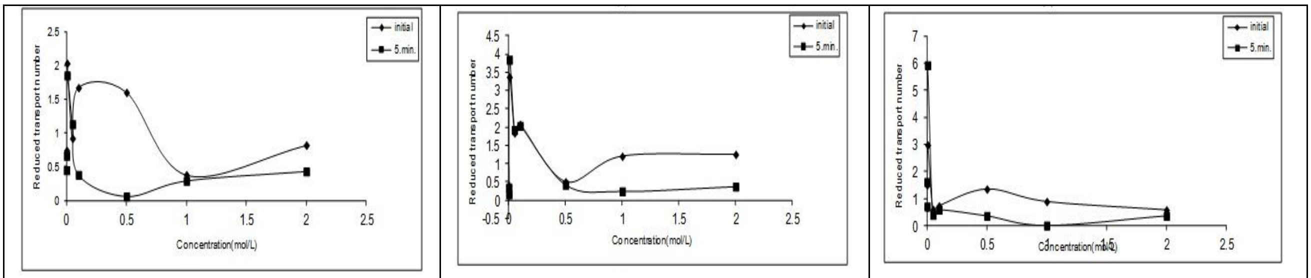
(a) (b) (c)

Figure 7 a. Mean reduced transport number values of K^+ in SA_3 membrane.
b. Mean reduced transport number values of K^+ in SA_3T membrane (supported C_1).
c. Mean reduced transport number values of K^+ in SA_3T membrane (supported C_2).



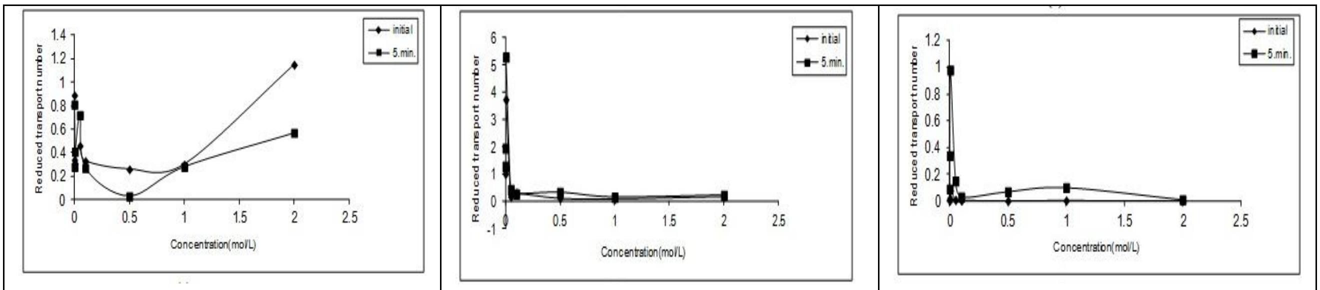
(a) (b) (c)

Figure 8 a. Mean reduced transport number values of Na^+ in SA_3 membrane.
b. Mean reduced transport number values of Na^+ in SA_3T membrane (supported C_1).
c. Mean reduced transport number values of Na^+ in SA_3T membrane (supported C_1).



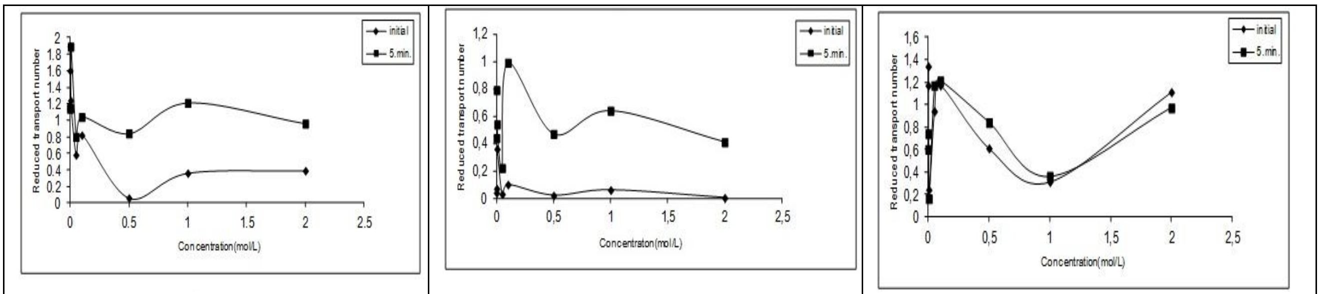
(a) (b) (c)

Figure 9 a. Mean reduced transport number values of Li^+ in SA_3S membrane.
b.Mean reduced transport number values of Li^+ in SA_3T membrane (supported C_2).
c.Mean reduced transport number values of Li^+ in SA_3T membrane (suppoted $C_{1)}$



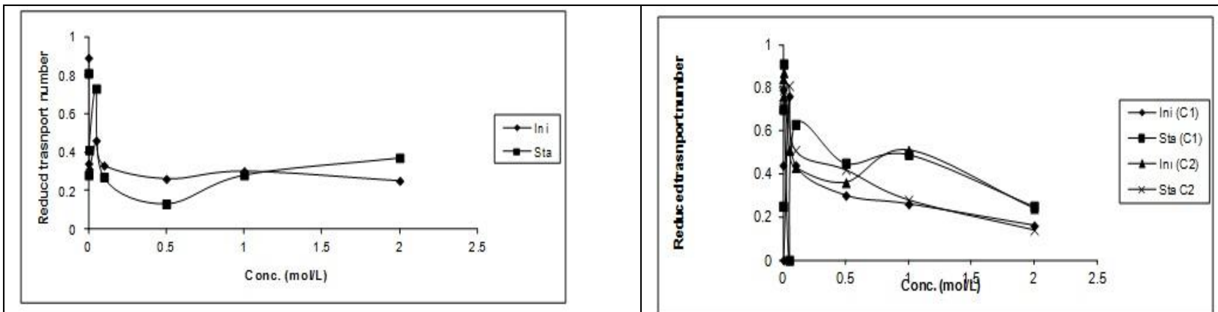
(a) (b) (c)

Figure 10 a. Mean reduced transport number values of Ca^+ in SA_3S membrane.[c]
b. Mean reduced transport number values of Ca^+ in SA_3T membrane (supported C_2).
c. Mean reduced transport number values of Ca^+ in SA_3T membrane (supported C_1).



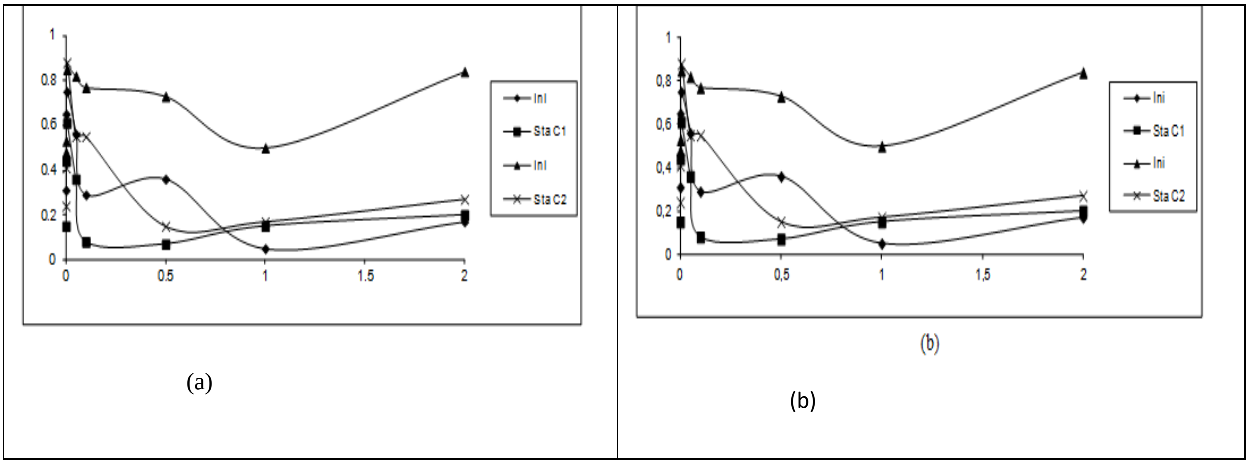
(a) (b) (c)

Figure 11. a. Mean reduced transport number values of Fe^{+3} in SA_3S membrane.
b. Mean reduced transport number values of Fe^{+3} in SA_3T membrane (supported C_1).
c. Mean reduced transport number values of Fe^{+3} in SA_3T membrane (supported C_2).



(a) (b)

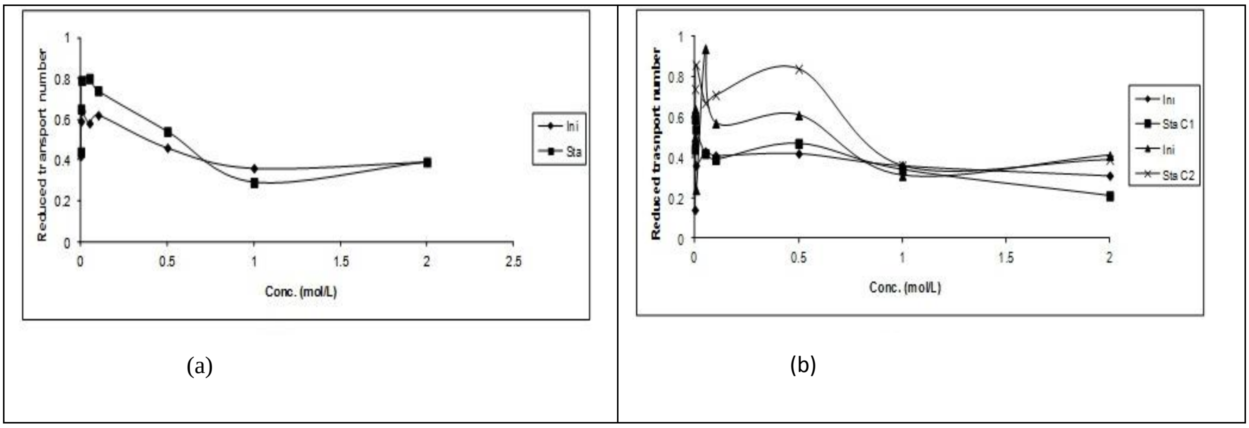
Figure 12 a. Mean reduced transport number values of K^+ in SA_3S membrane.
b. Mean reduced transport number values of K^+ in SA_3T membrane(supported C_1) and unsupported.



(a)

(b)

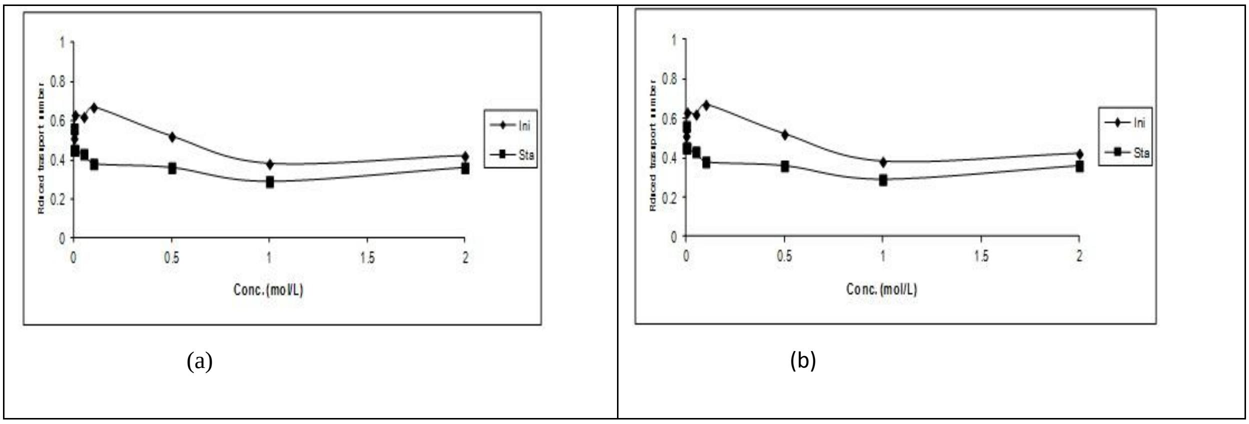
Figure 13 a. Mean reduced transport number values of Li^+ in SA_3S membrane.
b. Mean reduced transport number values of Li^+ in SA_3T membrane (supported C_2) and unsupported.



(a)

(b)

Figure 14 a. Mean reduced transport number values of Ca^{2+} in SA_3S membrane.
b. Mean reduced transport number values of Ca^{2+} in SA_3T membrane (supported C_2) and unsupported.



(a)

(b)

Figure 15 a. Mean reduced transport number values of Fe^{3+} in SA_3S membrane.
b. Mean reduced transport number values of Fe^{3+} in SA3T membrane (supportedC_1) and unsupported

4. CONCLUSION

* The variation of the transport numbers with the concentration for both surfaces is very close to each other.

* The concentration dependence shows differences which are remarkably high at the lower concentration than 0,005M. [9].

* Diffusion curves for SA_3T membrane whose one side is homogeneous and the other side heterogeneous show similar behaviors at different concentrations.

* Transport numbers are independent from concentration.

* In general, the stationary state values for the transport numbers show a little bit higher than the initial time values.

* In lower concentrations, reduced transport numbers of monovalent ions are larger than the divalent ions or multivalent ions.

* The difference between the stationary state and mean transport numbers for the two directions of the diffusion are generally larger in the case of the dense membrane.

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