Gazi University Journal of Science
GU J Sci
25(2):355-362 (2012)

ORIGINAL ARTICLE

The Donnan Potentials of Polysulfonated Cation Exchange Membranes

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Received: 20.04.2011 Revised: 23.01.2012 Accepted:24.01.2012

ABSTRACT

Membrane potentials of polysulfonated cation exchange membranes (unsupported polysulfone, SA_3S and polyester supported polysulfone, SA_3T) for KCl, NaCl and LiCl solutions using Ag/AgCl electrodes were measured. The measurements were carried out for, KCl SA_3S or SA_3T MCL, (M: K, Na and Li) systems. The concentration of salt (KCl) was kept constant in one side of the cell, C_1, at 1.10^{-2} M was changed in the other side of the cell C_2, from 1.10^{-4} to 2.0 M. The alteration graphs were drawn in order to find the potential values of membranes for (ln C_2) changes. Using the Donnan equation and the Teorrel Meyer Sievers theory, Donnan potentials were calculated theoretically. It was found that it had been dependent on ionic concentration of external solution. Donnan potential values determined for both membranes are parallel at 0.05 M concentration but there is deviation this value.

Keywords : Donnan potential, Diffusion potential, Membrane potential, Cation – exchange membranes, Effective fixed charge density, Permselectivity.

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1. INTRODUCTION

Ion-exchange membranes have been used in industrial processes such as electrodialysis, diffusion dialysis, electro-electrodialysis, membrane electrolysis, fuel cells, storage batteries, and others. Most of these studies have been focused to develop ion exchange membranes having high chemical, mechanical and thermal stabilities. The electrochemical properties of ion exchange membranes have been studied. Besides mechanical and chemical strengths of these membranes have been searched. It has been determined which one of them is more stable [1]. It has been reported that the non-uniformity of ion-exchange membranes directly affects many physical and chemical properties with advantages and disadvantages for their operational characteristics [2-6].

The electrochemical characterizations of ion exchange membranes are generally carried out by membrane potential or chronopotentiometry studies which is applied to assess the effect of charge of membranes on its transport properties arising due to electrolyte concentration and applied potential gradient or current, respectively. Membrane potential is an algebraic sum of two Donnan potentials and diffusion potential. It is determined by the partition of ions into the pore as well as the mobilities of ions within the membrane phase vis-a vis the external phase [4-10]. The transport of ions across the membrane can be related to the membrane potential which is caused by concentration gradient of an electrolyte impressed upon the membrane. The description of ion transport phenomena by examining the establishment of contribution of Donnan equilibrium at the interfaces between the membrane and the solution was proposed by Teorell-Meyers and Sievers [11-13].

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Membranes used in most of the separation processes under pressure (reverse osmosis, nanofiltration, and ultrafiltration) are nonsymmetrical membranes consisting, basically, of two layers from the same or different materials (asymmetric or composite membranes, respectively). In this study, the polysulfonated ion exchange membranes have the same homogeneous structural elements. These Supported membranes (SA_3T) are composite membranes which are made up a thin, dense active polysulfone layer and a thick, porous support (although a nonwoven structure is also commonly used for reinforcement). For this reason, the aim was to investigate the electrochemical behaviour of the membranes to find the get basic information for predicting membrane behaviour from the membrane potential measurements.

2. EXPERIMENTAL

Materials

The chemicals were obtained from Merck, Co. (Darmstadt, Germany). Two kinds of commercial cation exchange membranes, (polysulphone SA_3S homogenous and polysulphone with polyester support SA_3T heterogeneous), Gelman Sciences were, used. The basic specifications of both membranes are; ion exchange capacities, 1.522 and 1.132 meg.g^{-1} for SA_3S and SA_3T, respectively, pore size 0.45 μ *m* and thickness 152.4 μ *m*. The cation-exchange membranes were supplied in hydrogen form.

Membrane potentials

The membrane pretreatment process was described in previous work [14-15]. Before experiments, SA_3S and SA_3T membranes were conditioned with 0.01 M KCl. Membranes equilibrated were put in a cell consisting of two chambers having the volume of each was 50 ml and the effective membrane area was 7.07cm^2. The membrane was tightly clamped between two chambers by using silicone rubber rings; a magnetic stirrer was placed at the bottom of each half-cell to minimize concentration polarization of the membrane surfaces. The concentration of salt solution (KCl) was kept constant in one cell, C_1, at 1.0x10^{-2} mol/l and was changed in the other cell, C_2, from 1.0x10^{-4} to 2.0 mol/l. The electromotive force (ΔE) between the two sides of the membranes was measured by means of a DC Meter (nA Range 200 function mV) with Ag/AgCl electrodes. The solutions were renewed up to 0.10 mV till setting reproducible values. The solutions of both the compartments were vigorously stirred to ensure the return of equilibrium conditions in two solution-membrane interfacial zones.

Measurements were carried out using two different procedures:

i) The concentration of salt solution (KCl) was kept constant in one cell, C_1= 1.0x10^{-2} mol/l and changing other side, C_2= from 1.0x10^{-4} to 2.0 mol/l.

ii) 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 it gives different potential properties due to its heterogeneity. All of the experiments were carried out at 25 ^{0}C

Membrane potential, $\Delta\psi_m$, was determined from measured ΔE values by subtracting the electrode potential contribution.

Partition Coefficients

The partition coefficients were obtained from the data of sorption isotherms. After pretreatment and conditioning process, membrane samples were soaked in salt solution at 1 M solution concentrations to attain the equilibrium until no chloride ions were detected in the membranes for 24 h. They were then blotted quickly with filter paper and soaked in acid for 2 h. The amount of ions desorbed was determined by atomic absorption spectrophotometer (Pye Unicam 929), then the partition coefficient, *K*, for all metals was calculated using $K = \overline{C}/C$. Values of partition coefficient determined is shown in Table 1

3. RESULTS AND DISCUSSION

The electrical potential difference applied across the membranes develops due to the tendency of the oppositely charged ions to move with different velocities when the electrolyte solutions are separated by a charged membrane. This potential difference in unequal concentrations (C_1 and C_2) is called ñmembrane potential, $\Delta\psi_m$ ò. however when different electrolyte is used, it is called bi-ionic potential. The magnitude of the membrane potential depends on the electrical characteristic of the membrane along with the nature and concentration of the electrolyte solution used [5-6]. The membrane potential values, $\Delta\psi_m$ and Donnan potential values which are obtained versus ln C_2 at external solution concentration graphics are shown in figures1,2 and 3, respectively. According to Teorell-Meyer-Sievers (TMS) theory, the membrane potential can be considered as the sum of two Donnan potentials (one at each membrane solution interface) plus a diffusion potential in the membrane. These potentials are in Eq.(1) [16-18].

$$\Delta\psi_m = \Delta\psi_{diff} + \Delta\psi_{donn^1} + \Delta\psi_{donn^2} \qquad (1)$$

The expression for the above potentials is considered as follows;

$$\Delta\psi_{Don}\left(C_s \rightarrow m\right) = -\frac{RT}{F}\ln\frac{\left(\varpi C_x\right) + \left[\left(\varpi C_x\right)^2 + 4\left(Zk_{\pm}C_s\right)^2\right]^{-2}}{2K_{\pm}C_s} \tag{2}$$

$$\Delta\psi_{diff} = (RT/F)\left(\left[t_+/\left|z_+\right|\right] - \left[t_-/\left|z_-\right|\right]\right)\lambda n(C_1/C_2) \tag{3}$$

where $K_{\pm}$ is the partition coefficient of the salt, C_S is the concentration of salt in the external solution and C_X is the fixed charge concentration in the membrane; ω has a value of +1 or -1 for a positively or negatively charged membrane, respectively; *z* is the algebraic charge number; *RT* and *F* are gas constant and Faraday constant, respectively, *m,* is the membrane, $t_{\pm}$, represents the amount of current transported for one ion with respect to the total current crossing the membrane. For slightly charged membranes, when the external salt concentration is higher than the concentration of fixed charge in the membrane, the following approximation can be considered as [17] ;

$$\Delta\psi_m = \left(RT/F\right).\left[\left(1-2t_+\right) + \left(2g-1\right)\left(t_+t_-/g\right).\left(C_x/C_2\right)\right. \tag{4}$$

Where, *g* is concentration ratio ($g = C_1/C_2$) between two phases. If the parameter *g* is constant, Eq.(3) represents a linear relationship between $\Delta\psi_m$ and $1/C_2$ [20-21].

It can be seen from Figures 1-3 that the experimental values correspond to different parabolas. These parabolas are shifting to the left maximizely, when the constant concentration increases. When the membrane potential values are compared for SA_3S and SA_3T (supported side constant), the tendency of membrane potential values is similar to each other. In case of reverse direction for SA_3T (unsupported side constant), the membrane potential values exhibited different tendencies. From these results, it can be expressed that, some differences in $\Delta\psi_m$ values depending on the membrane surface in contact with constant concentration were observed. This effect is more obvious, particularly at lower concentrations. It was previously expressed that the fitting of the linear relationships allow the determination of the fixed charge concentrations and the average ion transport number in the charged membrane in Eq.(3) [18]. The determined values for the effective fixed charge concentration, C_X , in the membrane are given in Table 2. The calculated C_x values were found to be in the order KCl > LiCl > NaCl, for SA_3S, LiCl > KCl > NaCl for SA_3T (C_1 supported) and NaCl > LiCl > KCl for SA_3T (unsupported C_2).

Table 1: The calculated partition coefficient ($K_{\pm}$) values of salt solutions for both membranes.

Membrane	KCl	NaCl	LiCl
SA_3S	4.05	0.43	4.99
SA_3T	4.00	0.42	4.95

Table 2: The effective fixed charge concentration, C_x, and salt concentration in external solution for SA_3S and SA_3T membranes.

Electrolyte	C_x (Fixed charge concentration)			Cs (mol/L)		
	SA_3S	SA_3T (C_1)	SA_3T (C_2)	SA_3S	SA_3T (C_1)	SA_3T (C_2)
KCl	0.00081	0.000082	0.000082	0.001	0.0001	0.0001
NaCl	0.000031	0.000014	0.00029	0.0001	0.005	0.0001
LiCl	0.00047	0.00047	0.00047	0.0001	0.0001	0.001

Membrane potential data were obtained for both polysulfone cationï ion-exchange membranes with alkali salt chloride of unequal concentrations. The magnitude of membrane potential, $\Delta\psi$ is always greater than the corresponding diffusion potential which is showed in Table 3. The results correlate one of in previous studies [10] in which the magnitude of membrane potential was found to be greater than the corresponding diffusion potential. Furthermore, the results clearly show that the membranes are endowed with cation selectivity, since membrane potential is positive value in sign with respect to the higher concentration side.

Table 3. Diffusion potential values of cell (Ag,AgCl | MCl $C_S^{'}$) | M | KCl($C_S^{''}$) | Ag,AgCl).

Salts	Concentration (mol/L)	SA_3S	SA_3T ($C_S^{'}$ supported)	SA_3T ($C_S^{''}$ supported)
KCl	0.0001	0.114	0.106	0.101
	0.001	0.053	0.040	0.040
	0.005	0.014	0.006	0.009
	0.05	-0.031	-0.028	-0.029
	0.1	-0.054	-0.048	-0.047
	0.5	-0.096	-0.087	-0.085
	1.0	-0.091	-0.096	-0.106
	2.0	-0.130	-0.122	-0.127
NaCl	0.0001	0.104	0.088	0.090
	0.001	0.054	0.037	0.035
	0.005	0.017	-0.012	-0.013
	0.05	-0.037	-0.022	-0.035
	0.1	-0.050	-0.052	-0.050
	0.5	-0.093	-0.091	-0.087
	1.0	-0.106	-0.110	-0.097
	2.0	-0.126	-0.131	-0.122
LiCl	0.0001	0.103	0.087	0.081
	0.001	0.048	0.042	0.040
	0.005	0.005	-0.009	-0.001
	0.05	-0.035	-0.037	-0.038
	0.1	-0.051	-0.052	-0.051
	0.5	-0.091	-0.090	-0.094
	1.0	-0.116	-0.118	-0.112
	2.0	-0.133	-0.118	-0.127

The explanation for bi-ionic potential values in case of same co-ion presented but different counter ion by taking into account of the crossed ionic fluxes through cation exchange membrane was made by Makroni et all. They reported that the inter-diffusion process is completely controlled by the diffusion boundary layers (DBLs) of each counter ion flux which varies only with diffusion boundary layer thickness and is also independent of diffusion boundary layer thickness for the medium or higher concentrations [19]. In addition, they proposed two models. Both of them are homogeneous and heterogeneous type membranes. They are expressed that their experimental values were almost 10 times higher than that of theoretically similar results. For this reason, membrane potential values are found as the theoretical and experimental. These values are different from each other.

The interaction and movement of ions in membrane phase is very complex and difficult to elucidate in details and affected by some factors such as ionic concentration within the membrane charge density of membrane, composition of the solution, ionic fluxes, water content, etc. It is assumed that transport properties of the charged membranes depend strongly on the nature and density of the charges fixed to the membrane matrix. From this complexity, the functional groups of the membrane and the interaction between the membrane matrix and the ions in relation with the electrochemical behavior of the membranes need to be characterized. The used polysulphone membranes are truly micro porous ion-exchange membranes with controlled ion-exchange capacities. Excellent mechanical wet strength and also are especially designed suitable for trace metal analysis applications. In this study, the behavior of polysulphone membranes towards bi-ionic potential measurements was considered with their applications to various fields, particularly electrodialysis or metal preconcentration applications.

Table 4: Permselectivity, (P_{sm}) and the average cation transport number for SA_3S and SA_3T membranes.

Electrolyte	($P_{sm\ (+)(\%)}$)			The average cation transport number	
	SA_3S	SA_3T (C_1)	SA_3T (C_2)	SA_3S	SA_3T
KCl	77.6	78.7	73.8	0.86	0.83
NaCl	53.3	53.7	51.2	0.79	0.75
LiCl	38.3	37.2	39.6	0.71	0.66

The Donnan potential values were evaluated from the measured membrane potential values by using Eq.(1) in which the physical parameter values ($K_\pm$, C_x, C_s) were replaced and presented in Figures 1-3. It is known that Donnan potential is an equilibrium phenomenon and, in consequence, co-ions partially excludes from the membrane. In other words, the stronger the exclusion is the smaller the electrolyte uptake. Electroneutrality requires that the fixed charges should electrically balanced by counter ions which are in the excess of the co-ions in the ion exchanger. These counter ions cannot diffuse out (unless when being replaced by others) since the resulting charge transfer creates an electrical potential difference, the Donnan potential, which pulls them back. As the uptake of the electrolyte by the membrane increases with increasing concentration of the solution. In other words, the Donnan potential depends on ionic concentration and apparently seen in Figures 1(b), 2(b), (3b) the Donnan potential increases with increasing concentration of external solution by giving a good correlation coefficient higher than 0.9 value. The linear relationship between membrane potential and the external solution concentration was observed. The presented data agree with the assumption in terms of membrane potential due to the diffusion potential which is showed in Table 3. Donnan potential values which have been found for cation-exchange membranes (SA_3S and SA_3T) were parallel up to 0.1 M external electrolyte solution. The deviation from the parallel position has been related to the concentration proportion.

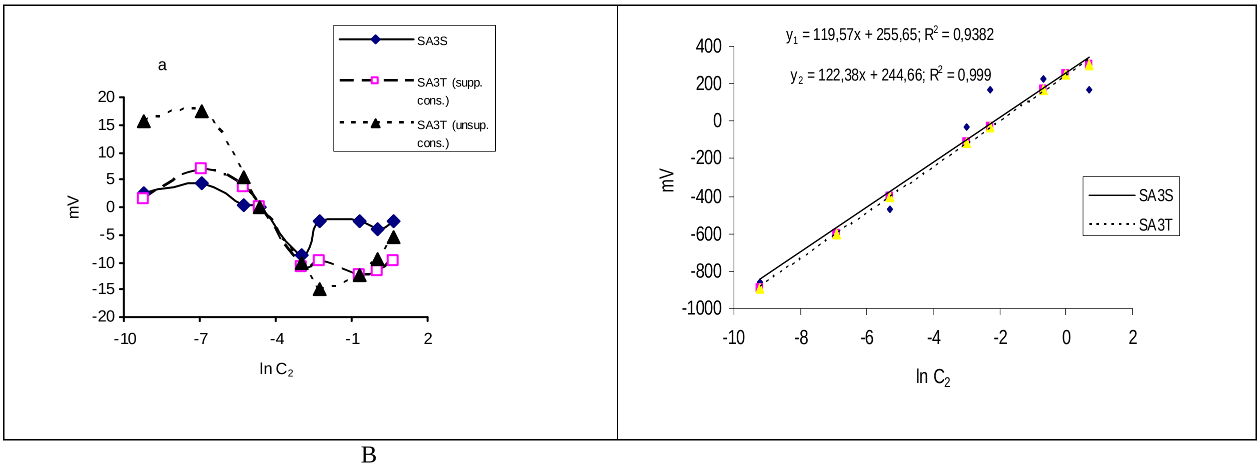

Figure 1. Membrane potential (a) and Donnan potential (b) values of SA_3S and SA_3T (supported and unsupported side was kept constant as 0.01 M KCl) with different concentration ranges. The data for SA_3T membrane was found to be same for both sides of the membrane.

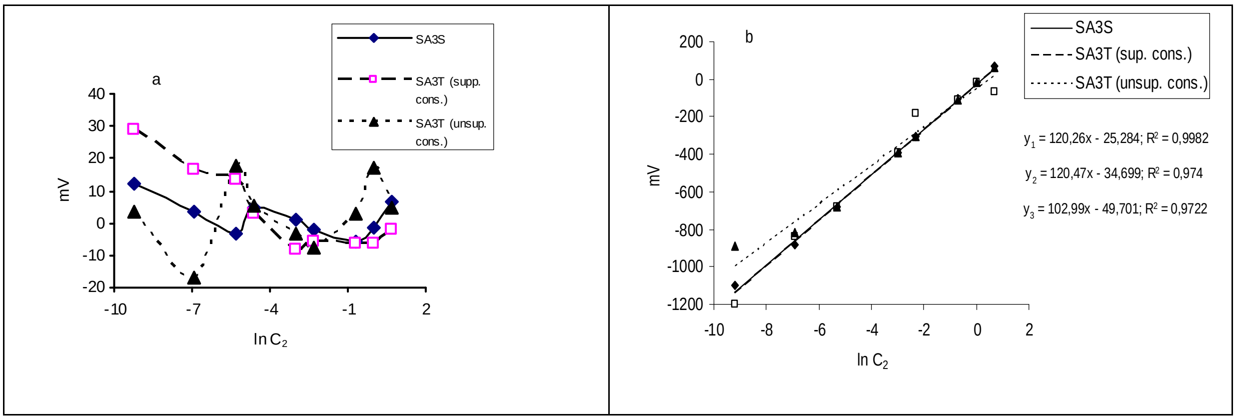

Figure 2. Membrane potential (a) and diffusion potential (b) values of SA_3S and SA_3T (supported and unsupported side was kept constant as 0.01 M KCl) while other side was NaCl at different concentration ranges.

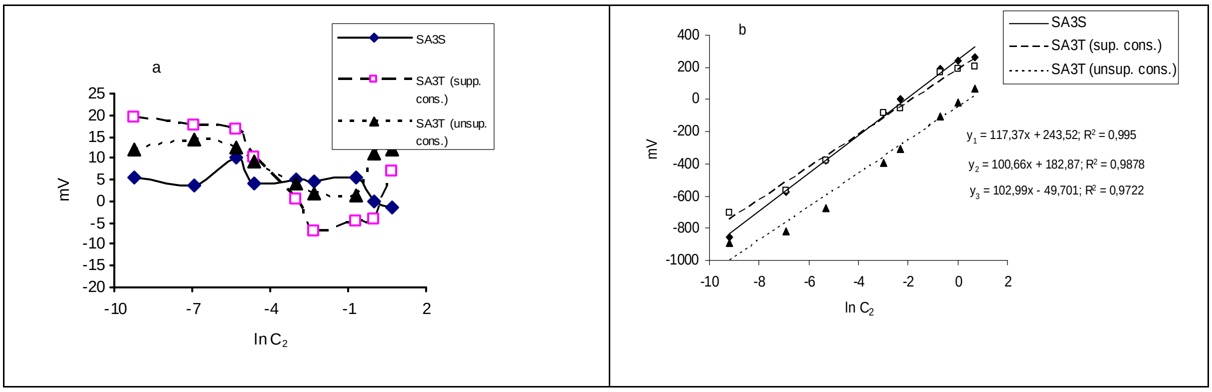

Figure 3. Membrane potential (a) and diffusion potential (b) values of SA_3S and SA_3T (supported and unsupported side was kept constant as 0.01 M KCl) while other side was LiCl at different concentration ranges.

Recently, the membrane potential model for an asymmetrical nanofiltration membrane was investigated by Xu et all. They developed a model in terms of improving TMS model, in which, a transient concentration at the interface was considered by assuming a contact factor to compensate the potential change caused by different layer characteristic properties of materials. The change of membrane potential in membrane is explained by contact factor with respect to the orientation of the membrane, giving a reasonable explanation for this, i.e., for positive orientation: where high concentration faces the dense layer, the contact factor weakens the effective concentration of fixed group concentration and thus lowers the membrane potential; for negative orientation, where the high concentration faces the porous sublayer, the contact factor strengthens the effective concentration of fixed group concentration and thus enhances the membrane potential [20]. In this study, the obtained Donnan potential values were changed from negative to positive orientation by increasing concentration difference.

Electrochemical or electrokinetic characterization of polysulfonated membranes may be identified by measuring of membrane potential which allows the determination of different characteristics of membrane parameters. The membranes used have same composition, but SA_3T has asymmetric characters, supported with polyester support. The influence of membrane asymmetry on transport parameters have been studied by carrying out measurements for two opposite external conditions by keeping of one side of the membrane phase concentration is constant. The obtained results show that the membrane asymmetry strongly affects membrane potential, which is attributed to the Donnan exclusion when the reversal experimental conditions was performed. In case of supported side concentration is constant; the membrane potential changes are practically similar for SA_3S membrane.

Permselectivity (P_{sm})

Ion selectivity of ion-exchange membrane is quantitatively expressed in terms of permselectivity which is a measure of the selectivity of counter ions over the co-ions in an ion exchange membrane. The permselectivity for counter ions in a cation exchange membrane can be obtained from the following equation [20].

$$P_{sm}(+) = (t_+ - t_+^o)/(1-t_+^o)\ )$$

Where t_+^0 represents the cation transport number in solution. The average permselectivity ($P_{sm}(+)$) can be obtained by taking (t_+) values for both electrolyte solutions.

The permselectivity values of membranes for C_2 (1x10^{-4}and 2 M) concentration ranges were calculated by using of Eq.(4) and the values are listed in Table 4. It can be seen that SA_3S and SA_3T membranes showed higher selectivity to K^+ ions and lower selectivity to Li ion. In addition, the obtained values of SA_3S and SA_3T (supported side constant) is found to be very close to each other, in case of SA_3T (unsupported side constant), the small differences were obtained due to the membrane asymmetry. Independent structure of membranes either homogeneous or heterogeneous. We remark also the influence of the electrolyte pair which is due essentially to the differences in the counter ion in their hydrated sizes. With regard to the hydrated radius of alkali ions, the hydrated radius of Li^+ is higher than that of Na^+ which is higher than that of K^+ [18]. Since these cations have the same electric charge, the higher the ion size the lower its mobility as well as its permselectivity. Then it is logical to obtain the permselectivity in the order $P_{KCl} > P_{NaCl} > P_{LiCl}$, respectively. The presented results are in agreement with the literature [7].

4. CONCLUSION

-The bi-ionic potential values in polysulfone membranes was studied by determining of membrane potential with KCl, NaCl and LiCl, at different concentrations, which allow the comparison of different transport parameters.

-Measurements of the bi-ionic potential through a cation exchange membrane were realized by keeping constant one concentration and varying the other. For the bi-ionic systems KCl / membrane / MCl systems, where, (M: K^+, Na^+, Li^+), the curves exhibit same tendency.

-The Donnan potential contributions for polysulfone cation exchange membranes shoved the same tendency giving a linear dependence with ln (C_1/C_2) changes.

-The effective fixed charge concentration, C_X in the membrane and the average transport numbers for monovalent ions were presented for both membranes.

ACKNOWLEDGEMENT

The authors are grateful for the financial support provided by the Coordinatorship of Selcuk University's Scientific Research Projects (SUBAP) Grant No. SU-2005/05701023

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