Potentiometric Determination of Fixed Charge Density and Permselectivity for Silver Thiosulphate membrane

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ABSTRACT

Effective fixed charge density of silver thiosulphate (parchment supported) membrane in contact with various 1:1 electrolyte solutions have been determined from membrane potential measurements. The methods used for the estimation of charge densities were: the Teorell-Meyer-Sievers method (T.M.S.), Altug and Hair method, and the recent theories for membrane potential of Kobatake et al. and Nagasawa et al. The values derived from different theories were almost the same, confirming thereby the validity of the recently developed theories of membrane potential for the evaluation of effective fixed charge density of the system under investigation. Apparent transference numbers of coions and permselectivities of the membrane-electrolytes have also been calculated. A method based on permselectivity values for determination of charge density was also used.

Keywords: Membrane potential, Fixed Charge density, Potentiometry.

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INTRODUCTION

The developments of new 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 [1–5]. The applicability of ion-exchange membranes may be limited without knowing the transport properties of membranes. Since the transport phenomena validate the performance of the membranes and hence provoked various industrial applications. Several membranes have been prepared using inorganic precipitates. However these inorganic membranes have sufficiently low chemical stability in acidic and alkaline medium due to dissolution of inorganic phosphate into inorganic salt [6]. A variety of membranes can be constructed whose structure is well defined and whose permeation mechanisms and particular parameters can be varied in a controlled manner. By correlating structure and ion permeation in such membranes, it should be possible to develop experimental criteria for determining the structure, and hence the mechanism of ion permeation through an unknown membrane. In an attempt to develop these criteria a number of inorganic precipitated membranes [7–9] have been prepared with ion exchange sites and have studied the extent to which their chemical and transport properties depend on various external forces such as different chemical

environments, temperature etc. The ionic selectivity of a membrane and the concentration range of the external salt solution in which its cationic behavior is shown both depend strongly on the fixed charge concentration of the membrane. The membrane fixed charge density can be determined using several methods: analytical titration [10], streaming potential measurements [11], and membrane potential measurements [12, 13]

In this paper, we describe the preparation of silver thiosulphate parchment supported membrane. The effective charge density which is considered as the most effective parameter controlling the membrane phenomena, have been determined by the different methods using membrane potential measurements.

MATERIALS AND METHODS

All the reagents used were of AR grade (BDH) without further purification and their solutions were prepared in deionized water.

Preparation of Membrane : Parchment supported silver thiosulphate membrane was prepared by the method of interaction described by Siddiqi et al. [14-17]. 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 h in a 0.2 M sodium thiosulphate solution at room temperature. The two solutions were interchanged and kept for another 72 h. 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 clamped between two half cells of an electrochemical cell. The membrane prior to the measurements had been aged by about 24 h immersion in 1 M in the testing electrolyte.

Membrane Potential Measurements : The potential developed by setting up a concentration cell of the type in scheme 1 described by Siddiqi et al. [18]. 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 σ = 10. The potentials were monitored by means of Knick Digital Potentiometer (No. 646). All measurements were carried out using a water thermostat at 25 ± 0.1^{o}C. The solutions were vigorously stirred by a pair of magnetic stirrer in order to be maintained uniform in both the half cells. The uni-univalent electrolytes examined were lithium chloride, sodium chloride, potassium chloride, and ammonium chloride.
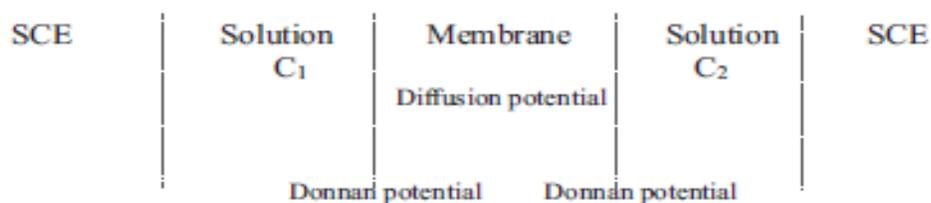
Scheme 1

RESULTS AND DISCUSSION

Evaluation of Effective Fixed Charge Density by Potentiometric Methods : The methods of T. M. S. [19-21], Altug and Hair [22], Kobatake et al [23, 24], and the most recent one of Nagasawa and co-workers [25, 26] were used for the evaluation of fixed charge density of silver thiosulphate membrane.

The inorganic precipitate membranes have the ability to generate potentials when they are used to separate electrolyte solutions of different concentrations [27-28]. This property is attributed to the presence of a net charge on the membrane due to absorption of anions or cations. The values of membrane potential measured in contact with different concentrations of various 1:1 electrolytes are given in table 1

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*

ωX : *Membrane charge density*

$\omega = \pm 1,$ *depending on the nature of the dissociated sites*

r_1 *and* r_2 : *Donnan distribution ratios at the two interfaces*

C : *Concentration in the membrane phase*

a : *External solution activity*

R : *Molar gas constant*

T : *absolute temperature of the system*

F : *Faraday constant*

α *and* β : *Parameters independent of salt concentration*

ΔE_{mr} : *Reduced membrane potential*

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

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

ϕX : *Thermodynamically effective fixed charge density of the membrane*

ϕ : *Fraction of counterions in the unbound form*

τ_- : *Mass fixed transference number of anion in the membrane*

P_s : *Permselectivity of the membrane-electrolye system*

Table 1. Observed membrane potential (mV) across $Ag_2S_2O_3$ membrane at 25 ± 0.1^{o}C

(C_2/C_1), M	Measured membrane potential (mV)			
	LiCl	NaCl	KCl	NH$_4$Cl
1.0/0.1	3	4	7	9
0.5/0.05	5	7	11	13
0.2/0.02	19	15	20	22
0.1/0.01	26	22	27	27
0.05/0.005	36	30	32	34
0.02/0.002	40	37	38	39
0.01/0.001	41	42	42	43
0.005/0.0005	44	43	43	44

The values of potentials observed across the membrane under investigation are low when these are used to separate concentrated solutions whereas it increases with dilution and reaches a maximum limit. This means that the membrane is negatively charged and selectivity increases with dilution. The negative charge may be attributed to the preferential absorption of a common anion between inorganic precipitate and the solution used for the preparation of the membrane. Two important factors which control electrolyte

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permeability through a membrane are charge on the membrane and its porosity. The fixed charged groups present on the membrane can be determined by potentiometric methods.

T. M. S. Method: The graphical method of Teorell, Meyer, and Sievers determines the fixed charge density X in equivalent per litter and the cation-to-anion mobility ratio (u_+/u_-) in the membrane phase. Theoretical concentration potentials (E_m) existing across the membrane are calculated with the help of equation (1) as a function of C_2, the concentration ratio (C_1/C_2) being kept at constant value for different mobility ratios.

$$E_m = 19.16\left[\log\frac{C_2\sqrt{4C_1^2 + X^2} + X}{C_1\sqrt{4C_2^2 + X^2} + X} + U\log\frac{\sqrt{4C_2^2 + X^2} + UX}{\sqrt{4C_1^2 + X^2} + UX}\right] \qquad (1)$$

Where:

$$U = \frac{u_+ - u_-}{u_+ + u_-} \qquad (2)$$

The values thus calculated are plotted (figure 1). The observed membrane potential values are also plotted in the same graph as a function of log ($1/C_2$). The experimental curve is shifted horizontally until it coincides with the theoretical curve. The extent of this shift gives (log X) and coinciding theoretical curve, the value for (u_+/u_-). The values derived in this way are given in table 2. This method gave satisfactory result for the fixed charge density evaluation, the values of which are found to be low and hence very difficult to determine by the usual exchange reaction.
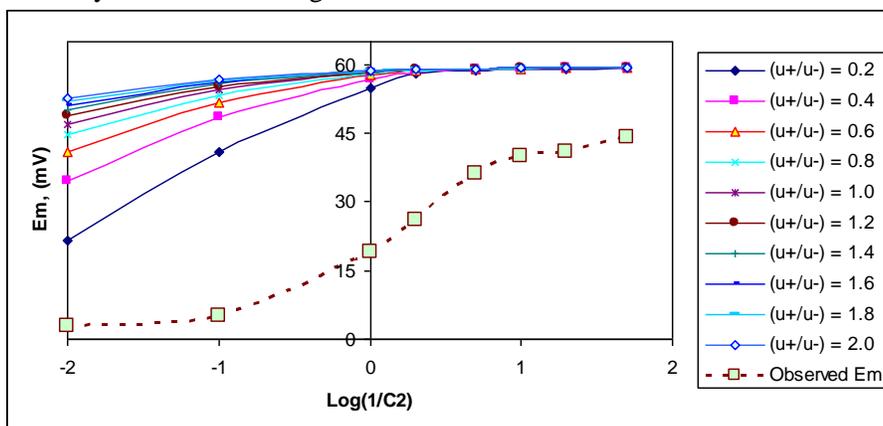

Figure 1. Membrane Potential vs. log ($1/C_2$) in contact with different concentrations of LiCl (TMS method)

Table 2. Comparison of charge density (eq. l^{-1}) by different methods for various electrolytes at $25\pm0.1^{\circ}$C

Electrolyte	TMS method	Altug & Hair method	Kobatake et al method		Nagasawa et al method
LiCl	0.018	0.020	0.016	0.025*	0.023
NaCl	0.023	0.030	0.024	0.028*	0.024
KCl	0.025	0.020	0.022	0.025*	0.021
NH$_4$Cl	0.026	0.030	0.023	0.026*	0.020

* From Perm selectivity values

Altug and Hair Method: In a modification of the type of plot of TMS, Altug and Hair evaluated ωX for glass membranes, choosing the solution values (u_+, u_-). In this method, a value of ωX was assumed and the distribution ratios (r_1, r_2) were calculated according to equation (3) for the given electrolyte concentrations C_1 and C_2, the theoretical membrane potential was then determined from equation (4) for each electrolyte and concentration range:

$$r = \frac{C}{a} = \sqrt{1 + \left(\frac{\omega X}{2a}\right)^2} - \frac{\omega X}{2a} \tag{3}$$

$$E_m = \frac{u_+ - u_-}{u_+ + u_-}\frac{RT}{F}\ln\left[\frac{a_1\left(r_1 u_+ + \dfrac{u_-}{r_1}\right)}{a_2\left(r_2 u_+ + \dfrac{u_-}{r_2}\right)}\right] + \frac{RT}{F}\ln\frac{r_2}{r_1} \tag{4}$$

By following the algebraic procedure, a series of theoretical curves were obtained and are shown by the solid lines in Figure 2. The experimental values of membrane potential observed for each electrolyte have been also plotted against concentration in the same figure (2). The theoretical curve which almost nearly coincides with the experimental one gives the value of fixed charge density. The values derived in this way are given in table 2
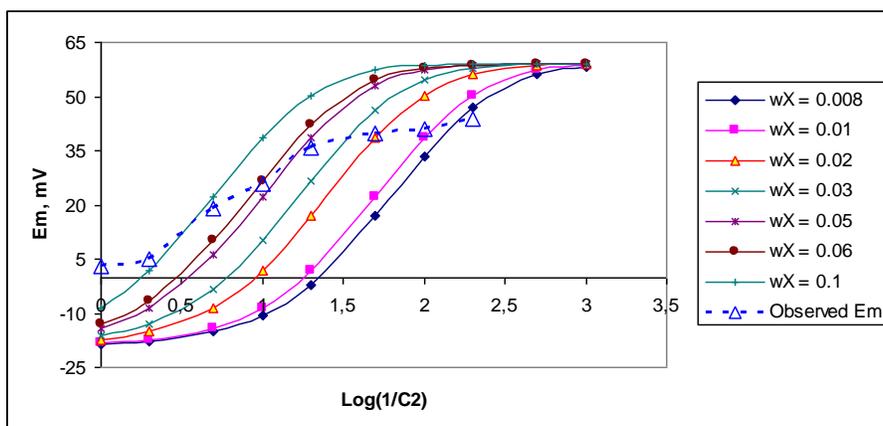

Figure 2. Membrane potential vs. log $(1/C_2)$ in contact with different concentrations of LiCl (Altug & Hair method)

Kobatake et al Method: Equation (5) indicates that a value of β and a relation between α and X can be obtained of a plot of $\left|\Delta E_{mr}\right|$ against C2 at fixed σ =10 (in the region of very low concentration – figure 3). The value of intercept is equal to $(1/\beta)$ ln σ, from which β may be evaluated.

$$\left|\Delta E_{mr}\right| = \left(\frac{1}{\beta}\right)\ln\sigma - \left(\frac{\sigma - 1}{\alpha\beta\sigma}\right)\left(1 + \frac{1}{\beta} - 2\alpha\right)\left(\frac{C_2}{X}\right) \tag{5}$$
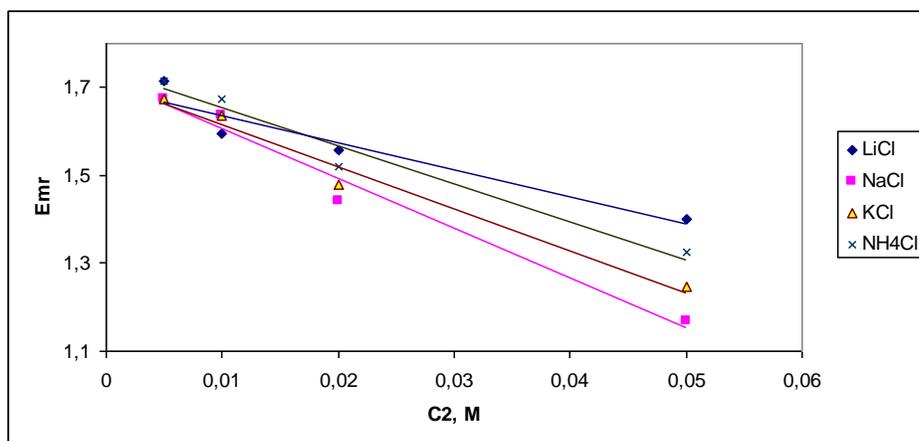

Figure 3. $\left|E_{mr}\right|$ vs C_2 in contact with different electrolytes (at low concentrations)

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Equation (6) indicates that the intercept of a plot of $(1/t_{-app})$ against $(1/C_2)$ at fixed $\sigma = 10$ allow the values of α to be determined. The values of the apparent transference number of co-ion calculated using equation (7) are given in Table 3. Plots of $(1/t_{app})$ against $(1/C_2)$ for various 1:1 electrolytes are given in Figure 4. From the value of intercept, α may be evaluated.

$$\frac{1}{t_{-app}} = \frac{1}{1-\alpha} \left[\frac{(1+\beta-2\alpha\beta)\,(\sigma-1)\,\alpha}{2\,(1-\alpha)^2\,\ln\sigma} \right] \left(\frac{X}{C_2}\right) \tag{6}$$

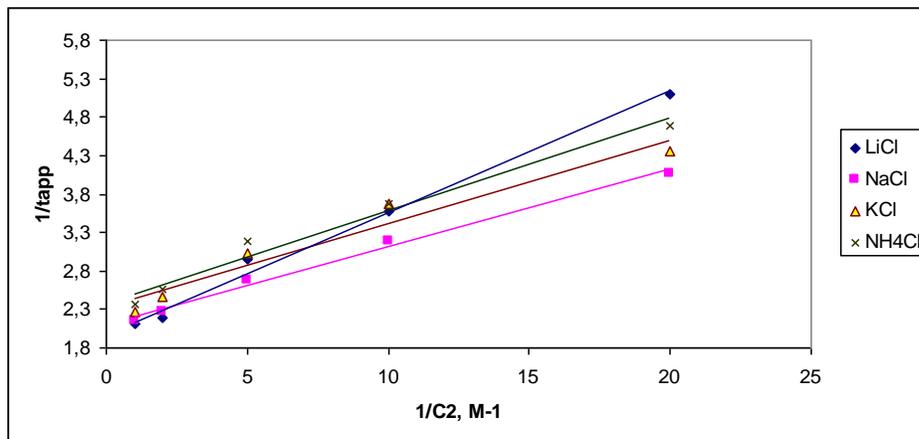$$\Delta E_{mr} = (1-2\,t_{-app})\ln\sigma \tag{7}$$

Figure 4. $1/t_{-app}$ vs. $1/C_2$ in contact with different electrolytes (at high concentrations)

Table 3. Apparent transference number of co-ions for various electrolytes at $25\pm0.1^{o}C$

(C$_2$/C$_1$) M	t$_{-app}$			
	LiCl	NaCl	KCl	NH$_4$Cl
1.0/0.1	2.11	2.15	2.27	2.36
0.5/0.05	2.18	2.27	2.46	2.56
0.2/0.02	2.95	2.68	3.02	3.18
0.1/0.01	3.57	3.18	3.68	3.68
0.05/0.005	5.10	4.07	4.35	4.69
0.02/0.002	6.17	5.35	5.59	5.88
0.01/0.001	6.54	6.90	6.90	7.30
0.005/0.0005	7.81	7.30	7.30	7.81

For the evaluation of X, there are two limiting cases: (a) in dilute range from the slope of equation (5). This value of X is designated by X_d; (b) in the concentrated range from the slope of equation (6). This value of X is designated by X_c. The values of α, β, X_d, and X_c derived in this way for membrane and 1:1 electrolytes are given in table 4

Table 4 . Values of α, β, X_d, and X_c for various electrolytes at $\sigma = 10$ by Kobatake et al method at $25\pm0.1^{o}C$

Electrolytes	α	β	X_d (eq. l^{-1})	X_c (eq. l^{-1})
LiCl	0.595	1.329	0.068	0.016
NaCl	0.525	1.300	0.059	0.024
KCl	0.570	1.314	0.056	0.022
NH$_4$Cl	0.581	1.286	0.055	0.023

In the present investigation with parchment-supported membranes, the X_d values are found to be higher than X_c values. It is also noted that the lower values of X (X_c) are closer to the charge density values determined by TMS method.

Evaluation of Effective fixed charge density from the Perm selectivity values: For the evaluation of effective fixed charge density, the various values of permselectivity P_s were calculated by substituting the values of α and t_{-app} in equation (8), the values of permselectivity are given in Table 4, and then plotted against log [$C_1+C_2/2$]. The results are shown in figure 5.

$$\frac{1}{\sqrt{4\zeta^2 + 1}} = \frac{1 - t_{-app} - \alpha}{\alpha - (2\alpha - 1)(1 - t_{-app})} \equiv P_s \tag{8}$$

Table 4. Values of perm selectivity P_s for various electrolytes at different concentrations at 25 ± 0.1^oC

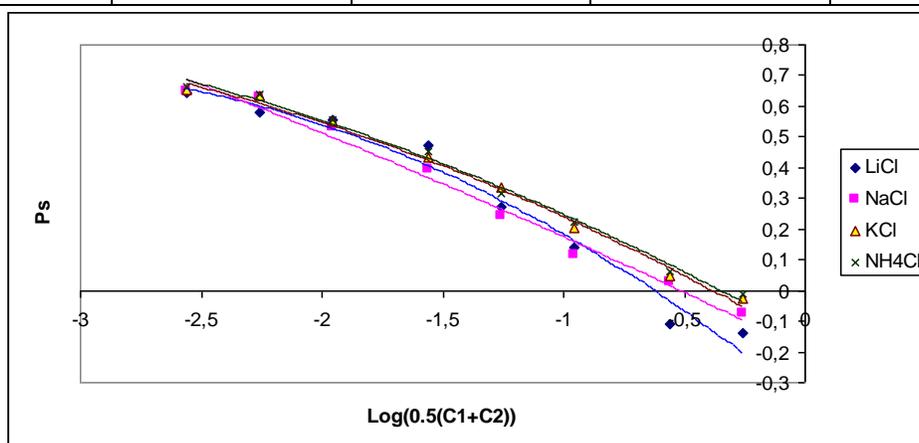| Concentrations (M)	LiCl	NaCl	KCl	NH$_4$Cl
1.0	-0.141	-0.077	-0.024	-0.010
0.5	-0.108	0.026	0.045	0.060
0.2	0.141	0.114	0.206	0.223
0.1	0.273	0.241	0.336	0.317
0.05	0.473	0.393	0.431	0.454
0.02	0.558	0.530	0.550	0.558
0.01	0.581	0.630	0.632	0.639
0.005	0.645	0.650	0.651	0.662

Figure 5. Plot of P_s against log [$C_1+C_2/2$] in contact with different concentrations for various electrolytes

The term ζ has already defined as:

$$\zeta = \frac{C}{\phi X} \tag{9}$$

When the average concentration C is equal to the effective fixed charge density ϕX, the value of P_s must give $\frac{1}{\sqrt{5}} = 0.448$ from left hand side equation (8). The corresponding concentration is obtained from the plot of P_s versus log C as given in Figure 5. This value of concentration is equal to the fixed charge density. The values are given for various electrolytes in table 2.

The method of Nagasawa and co-workers: Equation (10) predicts a linear relationship between ΔE_m and $1/C_2$ from which ϕX can be calculated.

$$-\Delta E = (\frac{RT}{F})\,(\frac{\phi X}{2})\,(\frac{\sigma-1}{\sigma})\,(\frac{1}{C_2}) \tag{10}$$

The values of ΔE_m were plotted against $1/C_2$ and a set of straight lines in Figure 6 point towards the correctness of the theory. The values of ϕX were calculated from the slope of the lines and are given in table 2.
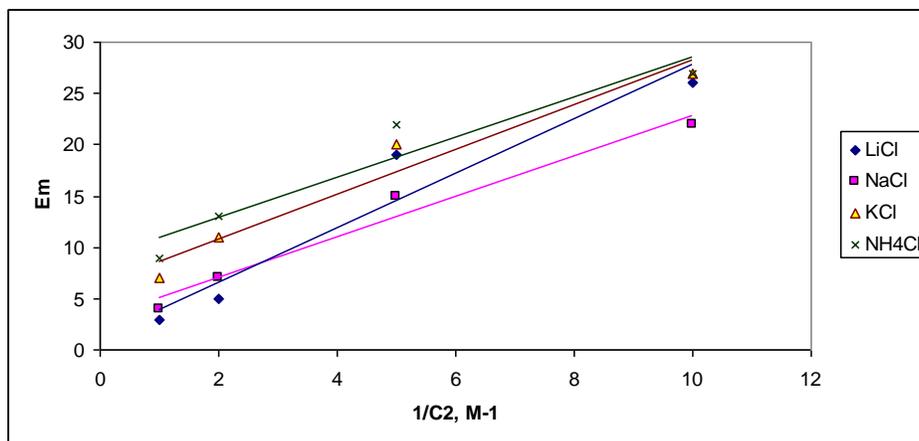

Figure 6. Plot of E_m against $1/C_2$ in contact with different concentrations for various electrolytes

APPLICATIONS

Perm selectivity values are useful for determination of charge density. The effective charge density which is considered as the most effective parameter controlling the membrane phenomena, have been determined by the different methods using membrane potential measurements.

CONCLUSIONS

The approach of TMS is unreliable to evaluate X for ion-exchange membranes which have a high concentration of fixed groups. It is not that unreliable for a membrane which has a low concentration of X, as found in this study, due to the fact the change in the values of the factor (u_+/u_-) is not as drastic as it is with membranes of high charge density. It is believed that the approach of Altug and Hair overestimated X in comparison to TMS method. The theoretical predictions from the Kobatake membrane potential equation is borne out quite satisfactorily by our experimental results and hence it may safely be concluded that Kobatake approach for charge density evaluation is the best among the existing of membrane potential.

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