Studies with Parchment Supported Membranes. VIII. Determination of the Thermodynamic Effective Fixed Charge Density of Barium Phosphate Membrane by Various Methods and Evaluation of Permselectivity

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The thermodynamic effective fixed charge density, the most important parameter governing transport phenomena in membranes, was estimated by methods of TMS, Altug and Hair and the most recent one of Kobatake based on the thermodynamics of irreversible processes. Kobatake's equation has also been utilized for the evaluation of permselectivity of membranes. The two limiting forms of his equation for dilute and concentrated ranges gave identical values of θ (charge density) for barium phosphate membrane. The theoretical predictions for membrane potential by the equation were borne out quite satisfactorily by experimental results obtained with the investigated membranes.

The theories of transport of charged or uncharged particles through membranes have been treated on the basis of the following: (a) the idealized theory of TMS[1-2] and its refinements,[3] (b) the pseudo thermodynamic approach due to Scatchard[4] and treatment based on the thermodynamics of irreversible processes,[5-8] and (c) a kinetic approach based on the theory of absolute reaction rates.[9-10] In the preceeding paper[11] we showed that the parchment supported membranes can generate potentials when they are used to separate electrolyte solutions of different concentrations. This is attributed to the presence of a net charge (negative in the case of 1: 1 electrolyte and positive in the case of 2: 1 or 3: 1 electrolyte) on the membrane probably due to the adsorption of anions or cations.[12-19] This communication deals with the evaluation of membrane fixed charge density on the basis of various approaches of TMS,[1-2] Altug and Hair[20] and Kobatake *et al.*[21-26] based on the thermodynamics of irreversible processes.

Experimental

The barium phosphate parchment supported membrane was prepared as described in part VII of this series.[11] The potential developed across the cell was measured by using a Pye Precision Vernier Potentiometer (No. 7568) at 25 °C (±0.1 °C).

S.C.E. | Solution | Membrane | Solution | S.C.E.
C_1 ↑ ↑ C_2
Donnan potential Donnan potential
←Diffusion potential→

Results and Discussion

The membrane potential data obtained with the barium phosphate parchment supported membrane in various 1: 1 electrolyte solutions are plotted as a function of log $(C_1+C_2)/2$ with the ratio ν of concentration C_2/C_1 fixed at 10 and are shown in Fig. 1.

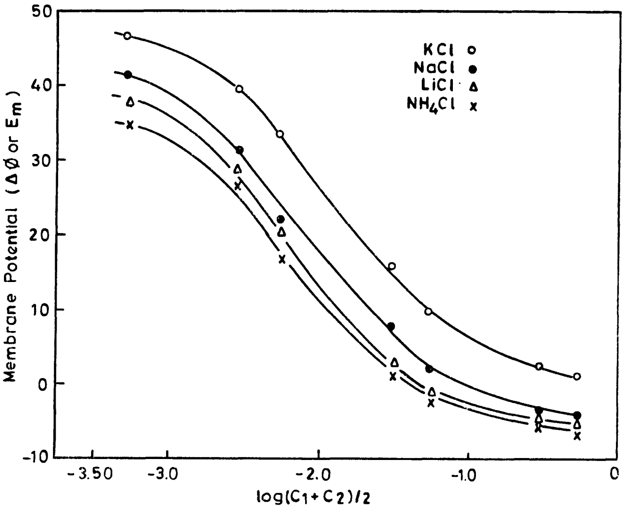

Fig. 1. Plots of observed potentials against log $(C_1+C_2)/2$ for various electrolytes with barium phosphate membrane.

The total membrane potential according to the Teorell[1] and Meyer-Sievers theories[2] consists of two Donnan potential at the two solution-membrane interfaces (π_1 and π_2) and a diffusion potential ($\phi_2-\phi_1$) arising from the unequal concentrations of the mobile ions at the two membrane surfaces. The membrane potential E_m or $\Delta\phi$ in millivolts according to TMS theory applicable to a highly idealized system is given by

$$E_\mathrm{m} = 59.16\left[\log\frac{C_1(\sqrt{4C_2^2+\bar{X}^2}+\bar{X})}{C_2(\sqrt{4C_1^2+\bar{X}^2}+\bar{X})} + \bar{U}\log\frac{\sqrt{4C_1^2+\bar{X}^2}+\bar{X}\bar{U}}{\sqrt{4C_2^2+\bar{X}^2}+\bar{X}\bar{U}}\right] \tag{1}$$

where $$\bar{U}=\frac{\bar{u}-\bar{v}}{\bar{u}+\bar{v}}$$

$\bar{u}$ and $\bar{v}$ are the mobilities of cation and anion, respectively, in the membrane phase (the bars refer to the parameters in the membrane phase), $\bar{X}$ is the effective charge on the membrane expressed in equivalents/litre of the imbibed solution. In order to evaluate this parameter for the simple case of 1: 1 electrolyte and membrane carrying a net negative charge of unity (*i.e.* $\bar{X}=1$) theoretical values for E_m were calculated as a function of C_2, the ratio ν of C_2/C_1 being kept at 10 for the different values of the mobility ratio $\bar{u}/\bar{v}$ and plotted as shown in Fig. 2.

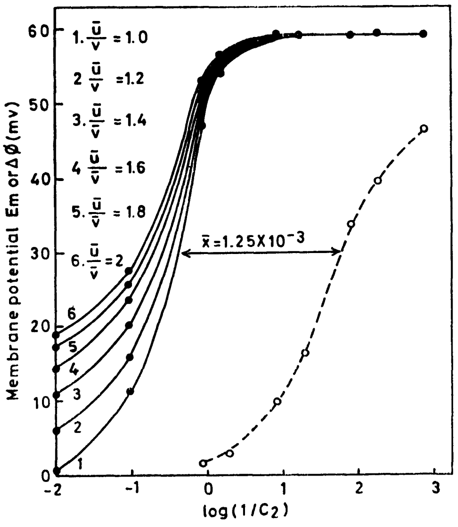

Fig. 2. Evaluation of membrane charge density x and the mobility ratio $\bar{u}/\bar{v}$ in the membrane phase. The different curves for different mobility ratio; ○. The observed value E_m for barium phosphate membrane for KCl are plotted against log $(1/C_2)$.

The observed membrane potential values for barium phosphate membrane and KCl electrolyte are plotted in the same graph as a function of log $(1/C_2)$. The experimental curve shifts horizontally and runs parallel to one of the theoretical curves. The extent of this shift gives log $\bar{X}$ and the parallel theoretical curve the value $\bar{u}/\bar{v}$. The values of $\bar{X}$ and $\bar{u}/\bar{v}$ so derived for the barium phosphate membrane and various 1 : 1 electrolytes are given in Table 1.

Table 1. Values derived for the membrane parameters $\bar{X}$ and $(\bar{u}/\bar{v})$

Membrane	Parameter	KCl	NaCl	LiCl	NH_4Cl
Barium phosphate	$(\bar{X})\times 10^3$ eq/l	1.259	3.162	1.995	1.995
	$(\bar{u}/\bar{v})$	1.0	1.0	1.0	1.0

In a modification of this type of plotting, Altug and Hair[20] evaluated $\bar{X}$ on the glass membrane chosing the aqueous electrolyte solution values for $\bar{u}$ and $\bar{v}$ and calculating the values for E_m assigning different values for $\bar{X}$. The total membrane potential E_{calcd} is given by

$$E_{\text{calcd}} = (\pi_1+\pi_2) + (\phi_2-\phi_1) \tag{2}$$

where

$$\pi_1 = -\frac{RT}{F}\ln r_1 \tag{3a}$$

$$\pi_2 = \frac{RT}{F}\ln r_2 \tag{3b}$$

r_1 and r_2 are the Donnan distribution ratios, which are determined by means of the equation

$$r = \left\{1+\left(\frac{w\bar{X}}{2a}\right)^2\right\}^{1/2} - \left(\frac{w\bar{X}}{2a}\right) \tag{4}$$

where a is the external solution concentration. The diffusion potential $(\phi_2-\phi_1)$ for 1 : 1 electrolyte is given by

$$(\phi_2-\phi_1) = \frac{u-v}{u+v}\,\frac{RT}{F}\ln\left\{\frac{a_1(r_1u+v/r_1)}{a_2(r_2u+v/r_2)}\right\} \tag{5}$$

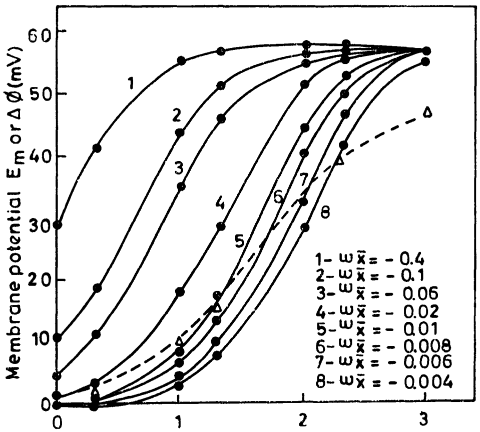

Fig. 3. Plots of membrane potential across barium phosphate membrane for KCl electrolyte of varying concentrations at fixed charge density against log $(1/C_2)$ (observed value are shown by brokenline).

where u and v are the cationic and anionic mobilities respectively, subscripts 1 and 2 referring to the solution on each side of membrane. Substitution in Eq. 2 gives

$$E_m = \frac{u-v}{u+v}\,\frac{RT}{F}\ln\frac{a_1\left(r_1u+\dfrac{v}{r_1}\right)}{a_2\left(r_2u+\dfrac{v}{r_2}\right)} + \frac{RT}{F}\ln\frac{r_2}{r_1} \tag{6}$$

Thus the membrane potentials are calculated by Eq. 6 for different values of fixed charge density $\bar{X}$. They are plotted in Fig. 3 as a function of the external solution concentration. The experimental values of membrane potential observed in the case of KCl for barium phosphate membrane are plotted against solution concentration. The theoretical curve which most nearly coincides with the experimental one gives the value of fixed charge density $\bar{X}$. The value of $\bar{X}$ thus calculated for KCl is given in Table 4.

Starting with the basic flow equations provided by the thermodynamics of irreversible processes Kobatake *et al.*[21] derived the following expression for the membrane potential $\Delta\phi$:

$$\Delta\phi = -\left(\frac{RT}{F}\right)\left[\frac{1}{\beta}\ln\frac{C_2}{C_1} - \left(1+\frac{1}{\beta}-2\alpha\right)\times\ln\left(\frac{C_2+\alpha\beta\theta}{C_1+\alpha\beta\theta}\right)\right] + \cdots \tag{7}$$

where

$$\alpha = \frac{l_+}{l_+ + l_-} \tag{8a}$$

and

$$\beta = 1 + (KF\theta/l_+). \tag{8b}$$

l_+ and l_- are the molar mobilities of $+ve$ and $-ve$ ions, respectively, defined in terms of the mass fixed frame of reference, K is a constant which is considered to depend on the viscosity of the solution and the structural details of the polymer net work of which the membrane is composed, θ is the charge density (in mol/cm^3) and F is the Faraday constant. These parameters have been assumed to be independent of salt concentration C_2 and C_1.

For the analysis of data, Eq. 7 can be used under two sets of conditions, two limiting forms thus being

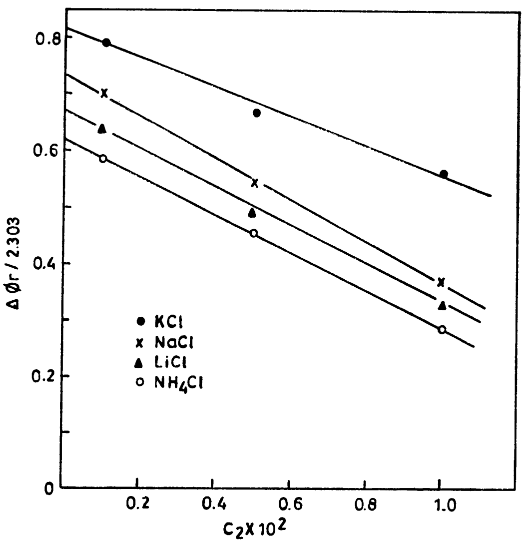

Fig. 4. $|\Delta\phi_r/2.303|$ *vs.* $C_2\times10^2$ plots for various electrolytes with barium phosphate membrane.

obtained: (a) when concentration C_2 becomes sufficiently small, (extreme dilute range) Eq. 7 can be expanded to give

$$|\Delta\phi_r| = \frac{1}{\beta}\ln\nu - \frac{\nu-1}{\alpha\beta\nu}\left(1+\frac{1}{\beta}-2\alpha\right)\frac{C_2}{\theta}+\cdots \qquad (9)$$

where $|\Delta\phi_r|$ is the absolute value of reduced potential defined by

$$|\Delta\phi_r| = \frac{F\Delta\phi}{RT}. \qquad (10)$$

Equation 9 indicates that the value of β and a relation between α and θ can be obtained by evaluating the intercept and initial slope of a plot for $|\Delta\phi_r|$ against C_2. Figure 4 shows plots for $|\Delta\phi_r|$ *versus* C_2 in the region of very low concentration determined for four electrolytes with barium phosphate membrane. The values of the intercepts for all electrolytes were equal to $(1/\beta)$ ln ν from which the values of β were evaluated (Table 2).

Table 2. Values of parameters α, β, and θ for various electrolyte with barium phosphate membrane at $\nu=10$

Electrolyte	α	β	θ
KCl	0.51	1.23	0.008
NaCl	0.46	1.33	0.0071
LiCl	0.44	1.53	0.0020
NH_4Cl	0.44	1.69	0.0070

(b) It is well-known experimentally that at fixed ν the inverse of an apparent transference number, *i.e.* t_{app}^{-}, for the co-ion species in a negatively charged membrane is proportional to the inverse of concentration C_2 in the region of high salt concentration. Here t_{app}^{-} is defined by the relation

$$|\Delta\phi_r| = (1-2t_{\mathrm{app}}^{-})\ln\nu \qquad (11)$$

Substituting for $\Delta\phi_r$ from Eq. 7 and expanding the resulting expression for $1/t_{\mathrm{app}}^{-}$ in powers of $1/C_2$ gives

$$\frac{1}{t_{\mathrm{app}}^{-}} = \frac{1}{(1-\alpha)} + \frac{(1+\beta-2\alpha\beta)(\nu-1)}{2(1-\alpha)^2\ln\nu}\left(\frac{\theta}{C_2}\right). \qquad (12)$$

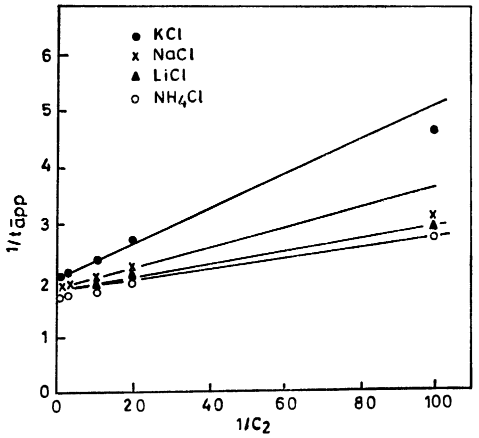

Fig. 5. $1/t_{\mathrm{app}}^{-}$ *vs.* $1/C_2$ plots for various electrolytes with barium phosphate membrane.

This indicates that intercept for a plot of $1/t_{\mathrm{app}}^{-}$ against $1/C_2$ at fixed ν allows the value of α to be determined. Plots of $1/t_{\mathrm{app}}^{-}$ against $1/C_2$ for various 1 : 1 electrolytes are shown in Fig. 5. The values of α are given in Table 2. There are two limiting cases for the evaluation of θ; (i) In the dilute range (1×10^{-3}M) using Eq. 9, the slope is given by

$$\frac{\nu-1}{\alpha\beta\nu}\left(1+\frac{1}{\beta}-2\alpha\right)\times\frac{1}{\theta}.$$

The graphical value of the slope determined from Fig. 4 is equated to the above equation, and the values of α and β are substituted. θ is thus evaluated, the value being designated as θ_d. (ii) In the concentration range (1.0 M) using Eq. 12, the slope is given by

$$\frac{(1+\beta-2\alpha\beta)(\nu-1)}{2(1-\alpha)^2\ln\nu}\times\theta.$$

The graphical value of slope determined from Fig. 5 is equated with the above expression and the values of α and β are substituted. θ is thus evaluated, the value being designated as θ_c.

In the present investigation with barium phosphate membrane, the two values of θ, *viz.* θ_c and θ_d, obtained from the opposite limits agree well with each other (Table 2) confirming the applicability of Kobatake's equation to this system. Also the value of α in Kobatake's treatment is defined by $u_+^0/(u_+^0+u_-^0)$ where u_+^0 and u_-^0 stand for the mobilities of cation and anion respectively in free solution. Thus, the value of α should be 0.5· KCl. The value of α obtained for KCl with barium phosphate membrane (Table 2) is 0.5. This implies that the assumption in the equation of Kobatake holds good for the barium phosphate membrane. It is evident that the constancy of the stoichiometric fixed charge density of the barium phosphate membrane is maintained, which is the basic assumption of the TMS theory[1–2] and its revised form given by Schlögl[3] and Kobatake *et al.*[21–26]

Comparison can be made between theoretical and experimental data and the applicability of Kobatake *et al.* equation to barium phosphate membrane can be tested by the following analytical technique suggested by Kobatake.

Equation 7 can be rewritten as

$$\frac{\nu-e^q}{e^q-1}=X \qquad (13)$$

with q and X defined by

$$q=\frac{[|\varDelta\phi_r|+(1-2\alpha)\ln\nu]}{1/\beta+(1-2\alpha)} \qquad (14a)$$

$$X=\frac{C_2}{\alpha\beta\theta}. \qquad (14b)$$

(The X is not the same as the one used in TMS or Altug and Hair method for the evaluation of charge density). Thus if Eq. 7 is valid, the values of log $(\nu-e^q)/(e^q-1)$ calculated from measured $\varDelta\phi$ and the given value of ν must fall on a straight line, which has a unit slope and passes the coordinate origin when plotted against log X as shown in Fig. 6, the theoretical predictions from the Kobatake *et al.* membrane potential equation are borne out quite satisfactorily by our experimental results with barium phosphate membrane.

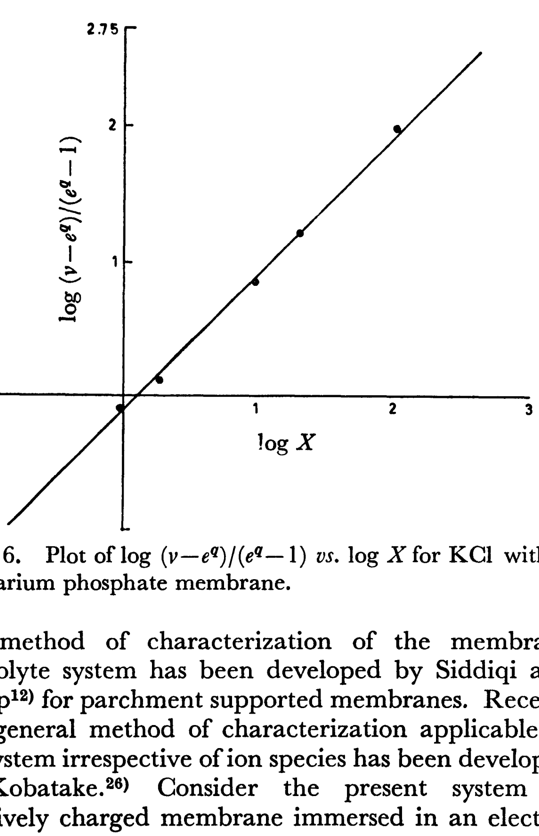

Fig. 6. Plot of log $(\nu-e^q)/(e^q-1)$ *vs.* log X for KCl with barium phosphate membrane.

A method of characterization of the membrane electrolyte system has been developed by Siddiqi and Pratap[12)] for parchment supported membranes. Recently a general method of characterization applicable to any system irrespective of ion species has been developed by Kobatake.[26)] Consider the present system of negatively charged membrane immersed in an electrolyte solution of average concentration C (*i.e.* $(C_1+C_2)/2$) for which Donnan equilibrium for small ions holds. The mass transference number τ_- of anions in the membrane is given by

$$\tau_-=1-\alpha\frac{(4\xi^2+1)^{1/2}+1}{(4\xi^2+1)^{1/2}+(2\alpha-1)} \qquad (15)$$

where ξ and α stand for the relative concentration defined by $C/\phi X$ and $u_+^0/(u_+^0+u_-^0)$ respectively.

On the other hand the apparent transference number of anions in the membrane, *i.e.* t_{app}^-, is defined from the derived membrane potential by the Nernst equation

$$\varDelta\phi=-\frac{RT}{F}(1-2t_{\text{app}}^-)\ln\frac{C_2}{C_1}. \qquad (16)$$

The difference between τ_- (in Eq. 15) and t_{app}^- (in Eq. 16) was less than 2% within a wide range of salt concentration.[26)] If τ_- is replaced by t_{app}^-, and C by $(C_1+C_2)/2$, Eq. 15 is applicable even when the concentration of the two sides of the membrane differs. Rearrangement of Eq. 15 leads to the following expression

$$\frac{1}{(4\xi^2+1)^{1/2}}=\frac{1-t_{\text{app}}^--\alpha}{\alpha-(2\alpha-1)(1-t_{\text{app}}^-)}\equiv P_s \qquad (17)$$

where P_s is a measure of permselectivity of the membrane electrolyte system. The value of P_s takes a value between zero and unity depending on the external salt concentration for a given system of a membrane and an electrolyte pair. P_s can be calculated from the data of the membrane potential, while the left hand side of Eq. 17 is a function of the relative concentration $\xi=C/\phi X$ or $(C_1+C_2)/2\phi X$. Thus the values of the right hand side should be independent of the mobilities of ion species involved. Equation 17 implies that the plot of P_s against $(1+4\xi^2)^{-1/2}$ should give a straight line of unit slope.

For the evaluation of the effective fixed charge density, another procedure suggested by Kobatake[26)] was also adopted for barium phosphate membrane. The various values of P_s were calculated by substituting the value of α (bulk) and t_{app}^- in Eq. 17 (*vide* Table 3) and then plotted against by log $(C_1+C_2)/2$. A curve was obtained as shown in Fig. 7 when the average concentration C, *i.e.* $(C_1+C_2)/2$, becomes equal to the effective fixed charge density ϕX, the value of ξ becomes equal

TABLE 3. VALUES OF PERMSELECTIVITY P_s FOR VARIOUS ELECTROLYTES OF BARIUM PHOSPHATE MEMBRANE AT DIFFERENT CONCENTRATIONS

Electrolytes	Concentrations (M)						
	1	0.5	0.1	0.05	0.01	0.005	0.001
KCl	0.05	0.06	0.18	0.29	0.58	0.67	0.80
NaCl	0.12	0.14	0.23	0.32	0.53	0.66	0.78
LiCl	0.24	0.26	0.29	0.29	0.58	0.71	0.79
NH_4Cl	−0.08	−0.06	0.0	0.06	0.30	0.47	0.60

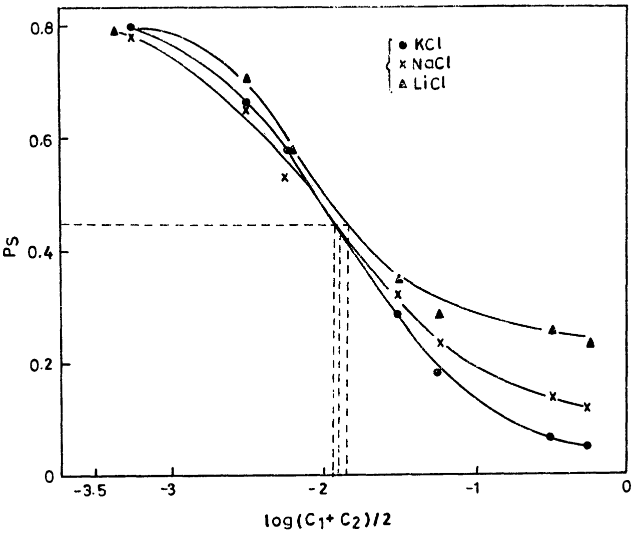

Fig. 7. Plots of P_s defined by Eq. 17 against log $(C_1+C_2)/2$ for various electrolyte with barium phosphate membrane.

TABLE 4. COMPARISON OF CHARGE DENSITY ($\phi\bar{X}$ OR $W\bar{X}$ OR $\bar{X}$) BY DIFFERENT METHODS FOR KCl

Membrane	TMS $\bar{X}$	Altug and Hair $W\bar{X}$	Kobatake's Eq. 12 θ^{*}	Eq. 9 θ^{*}	P_s vs. log $(C_1+C_2)/2$ $\phi\bar{X}$
Barium phosphate	0.1259×10^{-2}	0.800×10^{-2}	0.8×10^{-2}	2.0×10^{-2}	1.14×10^{-2}

$$\theta^{*} = \text{slope}\frac{2(1-\alpha)^2\ln\nu}{(1+\beta-2\alpha\beta)(\nu-1)\alpha} \qquad \theta^{*} = \frac{\nu-1(1+1/\beta-2\alpha)}{\text{slope }(\alpha\beta\nu)}$$

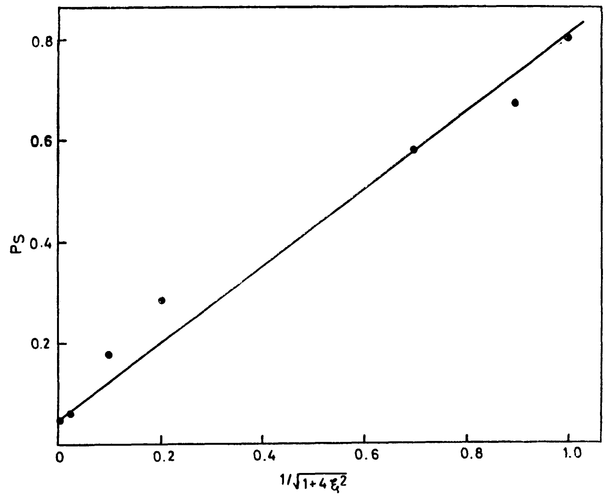

Fig. 8. Plots of P_s against $1/\sqrt{1+4\xi^2}$ for KCl electrolyte with barium phosphate membrane.

to unity, *i.e.* $C/\phi X=1$. Substituting this value of $\xi=1$ into $P_s=1/(4\xi^2+1)^{1/2}$, the value of P_s 0.448 is obtained. At this particular value of 0.448, the corresponding concentration is obtained from the curve P_s *versus* log C (Fig. 7). This value of concentration is equal to the fixed charge density (Table 4). The plot of P_s *versus* $(1+4\xi^2)^{-1/2}$ is drawn for barium phosphate membrane with KCl electrolyte is (Fig. 8). It is evident that the line passes through the origin with unit slope confirming the applicability of Kobatake's equation.

All the theories derived for the fixed charge membrane and used in these investigations give the effective fixed charge density θ or ϕX instead of X itself, when the charge density is evaluated from the data of membrane phenomena such as the membrane potential, ion permeability, electric resistance *etc.* Thus, the values of X do not differ from ϕX $(0<\phi<1)$. For the evaluation of true X the titration and isotopic methods were tried. The titration method proved very inconvenient and inaccurate. The isotopic method was discarded in view of strong ionic adsorption phenomenon exhibited by these systems. Consequently the potentiometric method was used.

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