

Table 2. Membrane potential values of 1:2 electrolytes for zirconium phosphoborate

Concentration of electrolyte, M	Membrane potential, V							
	MgCl ₂	CaCl ₂	SrCl ₂	BaCl ₂	Mg(NO ₃) ₂	Ca(NO ₃) ₂	Sr(NO ₃) ₂	Ba(NO ₃) ₂
0.001-0.01	0.021	0.025	0.017	0.034	0.019	0.020	0.0165	0.019
0.002-0.02	0.028	0.032	0.026	0.041	0.027	0.026	0.027	0.026
0.003-0.03	0.033	0.035	0.031	0.042	0.032	0.031	0.032	0.030
0.004-0.04	0.036	0.038	0.034	0.044	0.035	0.034	0.035	0.031
0.005-0.05	0.038	0.040	0.036	0.045	0.038	0.035	0.036	0.032
0.006-0.06	0.040	0.041	0.038	0.046	0.040	0.036	0.037	0.033
0.007-0.07	0.041	0.042	0.039	0.046	0.042	0.037	0.038	0.034
0.008-0.08	0.042	0.043	0.040	0.047	0.042	0.038	0.040	0.034
0.009-0.09	0.042	0.043	0.40	0.047	0.042	0.038	0.040	0.035
0.01-0.1	0.043	0.042	0.038	0.048	0.041	0.039	0.039	0.036

The ionic perm selectivity of membrane is also expressed quantitatively, based on migration of counter ions through cation exchange membrane [11,16,18-26]:

$$P_s = (\bar{t}_+ - t_+) / (1 - t_+)$$

Where \bar{t}_+ refers to the value of transport number in the membrane and t_+ is the transport number of counter ions in solution [27].

Ion exchange capacity of ZrPB

The ion exchange capacity of zirconium phosphoborate was determined for some monovalent and bivalent cations like Na⁺, K⁺, Mg²⁺ and Ca²⁺ cations and is given in Table 3.

Table 3. Ion exchange capacity of zirconium phosphoborate for some alkali and alkaline earth metals

Sr. No.	Metal ion	Salt solution used	Ion-exchange capacity, eq kg ⁻¹
1	Na ⁺	NaCl	0.29
2	K ⁺	KCl	0.58
3	Ca ²⁺	CaCl ₂	0.52
4	Mg ²⁺	MgCl ₂	0.32

The ion exchange capacity of ZrPB has been found in the order K⁺ > Na⁺ and Ca²⁺ > Mg²⁺. These results suggested that the ion exchange capacity decreases as the radii of hydrated metal ions increase.

The magnitude of membrane potential depends on:

1. Adsorption of anions of diffusing electrolyte on membrane surface
2. Exchangeability of cations
3. Size of cations
4. Diffusion potential across the membrane

Higher membrane potential for lithium is because of its small size and high positive field around it, hence, it establishes higher potential across the charged membrane. Higher the potential, higher is the permeability [28] as observed in our experiments in the concentration range (0.01 to

0.06 M). The trend in the membrane potential and hence greatest permselectivity for lithium ions is because ion mass transfer coefficient through the ion-exchange membrane increases as a function of ion size [29].

Ionic radii and hydrated ionic radii

Smaller the size of the alkali metal less is the ionic radius. As the size increases from top to bottom, ionic radii increase. The extent of hydration depends upon the size of the ion. Smaller the size of the ion, more highly it is hydrated and greater is its hydrated ionic radius and less is its ionic mobility (conductance). The radii and mobility of alkali metal ions are given in table 4.

Table 4. Values of ionic radii, hydration numbers, hydrated ionic radii and ionic mobility of alkali metal ions

Metal ions	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
Ionic Radius, pm	76	102	138	152	167
Hydration Number	25.3	16.6	10.5	10.0	9.9
Hydrated Radius, pm	340	276	232	228	228
Ionic Mobility	33.5	43.5	64.5	67.5	68

Transport Numbers

The transport number in exchanger phase is calculated from the slope of equation (1). The transport numbers and perm selectivity values of 1:1 halides and nitrates, and the transport numbers of 1:2 halides and nitrates are given in the Table 5 and 6, respectively.

Table 5. Transport numbers and perm selectivity values at mean concentration for 1:1 electrolytes

Mean concentration of electrolyte, M	Transport No. (\bar{t}_+)						Perm selectivity (P_s)					
	Metal halide electrolyte			Metal nitrate electrolyte			Metal halide electrolyte			Metal nitrate electrolyte		
	LiCl	NaCl	KCl	LiNO ₃	NaNO ₃	KNO ₃	LiCl	NaCl	KCl	LiNO ₃	NaNO ₃	KNO ₃
0.0055	1.08	0.53	0.75	0.45	1.15	0.8	1.12	0.23	0.51	0.179	1.247	0.609
0.011	1.44	0.71	0.67	0.74	1.17	0.85	1.65	0.52	0.35	0.613	1.280	0.706
0.0165	1.66	0.75	0.89	0.81	1.21	0.92	1.98	0.59	0.71	0.717	1.344	0.843
0.022	1.85	0.86	0.93	0.85	1.4	0.94	2.26	0.77	0.86	0.777	1.656	0.882
0.0275	2.02	0.89	0.97	0.92	1.47	0.97	2.51	0.82	0.94	0.881	1.771	0.941
0.033	2.06	0.91	0.99	0.94	1.55	1.03	2.56	0.85	0.98	0.911	1.899	1.059
0.0385	2.09	0.93	0.98	1.1	1.6	1.01	2.6	0.89	0.96	1.147	1.979	1.02
0.044	2.14	0.95	1.01	1.1	1.62	1.04	2.67	0.91	1.02	1.147	2.01	1.078
0.0495	2.16	0.96	1.02	1.12	1.66	1.05	2.7	0.93	1.04	1.176	2.075	1.098
0.055	2.22	1.2	0.39	1.13	1.71	1.03	2.78	0.32	0.19	1.190	2.145	1.059

It is observed that the transport numbers increase with increase in concentration of the electrolytes. This may be due to the fact that with increase in average concentration of the electrolyte, the number of counter ions interacting with the membrane surface increase leading to enhanced Donnan exclusion responsible for increase of transport numbers. The obtained results are in contrast with the Donnan equilibrium theory. The transport numbers tend to stabilize up to a mean concentration of 0.045 M. Thereafter, the values of transport numbers and permselectivity

tend to stay constant. This is due to concentration polarization phenomenon at high concentration resulting in increased co-ion percolation and hence resisting further increase in transport number of cations.

Table 6. Transport numbers at mean concentration for 1:2 electrolytes

Mean concentration of electrolyte, M	Transport No. \bar{t}_+							
	MgCl ₂	CaCl ₂	SrCl ₂	BaCl ₂	Mg(NO ₃) ₂	Ca(NO ₃) ₂	Sr(NO ₃) ₂	Ba(NO ₃) ₂
0.0055	1.43	1.60	1.25	2.01	1.34	1.39	1.25	1.34
0.011	1.74	1.92	1.65	2.32	1.70	1.65	1.65	1.65
0.0165	1.96	2.05	1.87	2.37	1.90	1.87	1.87	1.83
0.022	2.09	2.2	2.0	2.45	2.0	2.0	2.00	1.87
0.0275	2.18	2.27	2.09	2.50	2.18	2.05	2.09	1.92
0.033	2.27	2.31	2.18	2.54	2.27	2.09	2.18	1.96
0.0385	2.31	2.36	2.23	2.54	2.35	2.14	2.23	2.0
0.044	2.36	2.40	2.27	2.59	2.35	2.18	2.27	2.0
0.0495	2.36	2.40	2.27	2.59	2.35	2.18	2.27	2.05
0.055	2.35	2.36	2.18	2.56	2.31	2.16	2.18	2.02

Fixed charge density

The electrical character of a membrane is expressed in terms of fixed charge density. This fixed charged density of zirconium phosphoborate membrane for 1:1 electrolytes has been evaluated by using Kobatake's equation [30] and is given in Table 7.

Table 7. Values of parameters α , β and \bar{X} for zirconium phosphoborate membrane

Electrolyte	α	β	\bar{x}
LiCl	0.80	2.04	0.0075
NaCl	0.56	4.79	0.0078
KCl	0.60	3.83	0.0047
LiNO ₃	0.56	4.42	0.0072
NaNO ₃	0.68	2.55	0.0024
KNO ₃	0.62	4.34	0.0011
MgCl ₂	0.67	0.34	1.51
CaCl ₂	0.69	0.23	2.22
SrCl ₂	0.70	0.26	1.94
BaCl ₂	0.75	0.60	0.61
Mg(NO ₃) ₂	0.57	6.22	.0036
Ca(NO ₃) ₂	0.57	1.15	0.49
Ba(NO ₃) ₂	0.62	0.76	0.67
Sr(NO ₃) ₂	0.61	0.13	4.69

When negatively charged membrane separates solutions of electrolyte of different concentrations, the membrane potential is given by:

$$E_m = -\frac{RT}{F} \left[\frac{1}{\beta} \ln \frac{C_2}{C_1} - \left(1 + \frac{1}{\beta} - 2\alpha \right) \ln \frac{C_2 + \alpha\beta\bar{X}}{C_1 + \alpha\beta\bar{X}} \right] \quad (3)$$

where $\alpha = \frac{u}{u+v}$ and $\beta = 1 + \frac{KF\bar{X}}{u}$

E_m = membrane potential difference,

u and v = molar mobilities of cation and anion, respectively,

K = a constant depending on the solution viscosity,

\bar{X} = fixed charged density,

F = faraday constant.

In order to evaluate α , β and \bar{X} , Kobatake has derived two useful limiting forms, (a) and (b) of equation (3)

a) When $C_2 \ll \delta$, equation (3) may be written as:

$$|E_m^\sigma| = \frac{1}{\beta} \ln \delta - \left(\frac{\delta - 1}{\alpha\beta\delta} \right) \left(1 + \frac{1}{\beta} - 2\alpha \right) \frac{C_2}{\bar{X}} \tag{3a}$$

where, $|E_m^\sigma|$ = absolute value of membrane potential given by

$$|E_m^\sigma| = \frac{FE_m}{RT} \quad \text{and} \quad \delta = \frac{C_2}{C_1}$$

From the plot of $|E_m^\sigma|$ vs. C_2 in low concentration region, a straight line with an intercept equal to $1/\beta \ln \delta$ is obtained (Figure 1). Thus β can be calculated.

b) At fixed δ , inverse of apparent transport number $1/\bar{t}_{+app}$ for a coion species in a negatively charged membrane, varies linearly with the inverse of concentration C_2 at higher electrolyte concentrations, where $1/\bar{t}_{+app}$ is defined as

$$|E_m^\sigma| = (1 - 2\bar{t}_{+app}) \ln \delta$$

Substituting for E_m^σ in equation (3) and expanding resultant for expression for $1/\bar{t}_{+app}$ in power of $1/C_2$ gives

$$\frac{1}{\bar{t}_{+app}} = \frac{1}{1-\alpha} + \frac{(1+\beta-2\alpha\beta)(\delta-1)\alpha}{2(1-\alpha)^2 \ln \delta} \left(\frac{\bar{X}}{C_2} \right) \tag{3b}$$

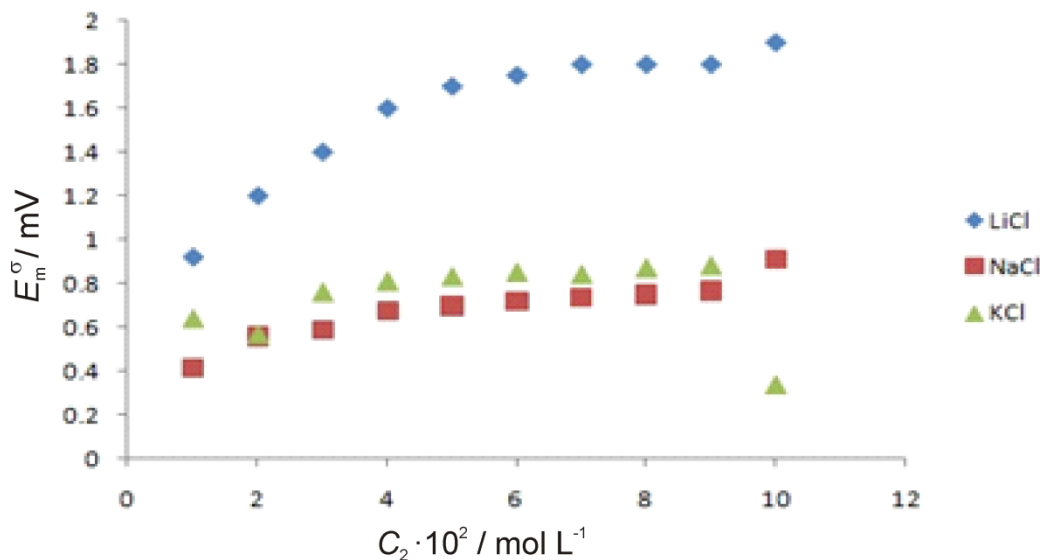


Figure 1. Variation of membrane potential with the concentration of electrolyte

From equation (3b), it is clear that a plot of $1/\bar{t}_{+app}$ vs. $1/C_2$ (Figure 2) at fixed δ value should be a straight line with an intercept equal to $1/(1-\alpha)$, from where α can be calculated.

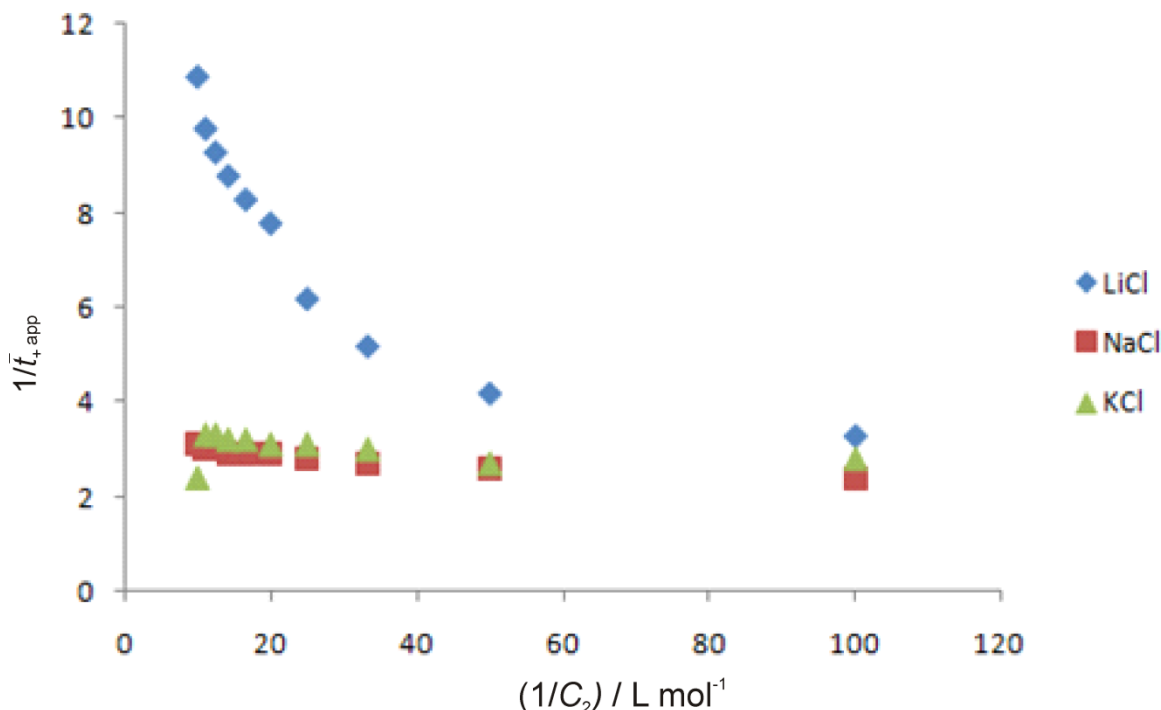


Figure 2. Variation of apparent transport number with reciprocal of concentration

For determining the fixed charge density \bar{X} in dilute concentration range, the value of slope determined from the plot of $|E_m^\sigma|$ vs. C_2 plot was equated with the slope of equation (3a). α and β being known earlier, \bar{X} can be calculated.

$$\text{Slope} = \frac{\delta-1}{\alpha\beta\delta} \left(1 + \frac{1}{\beta} - 2\alpha \right) \frac{1}{\bar{X}} \quad (4)$$

Apparent transport number $1/\bar{t}_{+app}$ indicates transport number of a metal ion in the exchanger whereas the transport number of the same metal ion in solution phase is represented by t_+ . As cited in the literature [31], transport numbers of alkali metal ions in an aqueous system generally increase sharply with initial increase in concentration in low concentration range and then become constant at higher concentration. This is true for all alkali metal ions including Li^+ , Na^+ and K^+ . As shown in Figure 2, the apparent transport numbers for Na^+ and K^+ do not change at all, whereas for Li^+ , an appreciable linear increase in trend is observed, which indicates that the ion exchanger matrix is selective for some metal ions. The selective behavior of the ion exchange membrane for Li^+ ions may be either due to steric or electronic reasons. This can't be due to steric reasons because hydrated radii of all the alkali metal ions are almost of the same size. Li^+ in dehydrated form has large charge to radius ratio as compared to that of Na^+ and K^+ .

The different trends of transport number in solution and in membrane phase confirm that the membrane is highly selective for Li^+ over Na^+ and K^+ . This property of the membrane can also be generalized for transition metal ions as well because metal ions of lanthanide series are also different from one another due to their electronic properties while their ionic radii (steric factor) do not change much.

It is observed that \bar{t}_{+app} decreases with increase in mean concentration of the lithium chloride electrolyte. These membrane permeate interactions indicate crystalline morphology [32], being more in amorphous and less in crystalline membranes. The low values indicate very low degree of crystallinity of exchanger material.

The observed values (Table 7) of fixed charge density \bar{X} are much lower than those expected from the fixed charge concentration of the exchanger. It indicates that larger part of internal fixed charge remains inactive. It may be due to the reason that active fixed charges in these membranes are essentially those of external surface of grain. As observed in Table 7, the magnitude of \bar{X} values for alkali metal nitrates is lower than for alkali metal chlorides. Hence, the trend in fixed charge density observed for halide and nitrate salts indicates that Donnan exclusion is more applicable for halide salts than for nitrate salts

Conclusions

The present investigation shows that ion exchange capacity of the ion exchanger decreases with the increase in the radii of hydrated metal ions. The transport numbers increase with increase in average concentration of the electrolyte due to enhanced Donnan exclusion at low electrolyte concentration. The transport numbers decrease at high concentration due to concentration polarization phenomenon. Hence, zirconium phosphoborate membrane shows better characteristics at lower concentrations (up to 0.045 M) beyond which no appreciable change in activity of the membrane is noticed and remains almost constant. The proposed ion exchange membrane behaves much more selectively for alkaline earth metal ions than alkali metal ions as observed from their respective fixed charge density values.

Acknowledgement: SK and PPS gratefully acknowledge Punjab Technical University (PTU), Jalandhar for permission to work on the project. SKM is thankful to Director, Thapar University, Patiala for the support.

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