Studies with Parchment Supported Membranes. VII. Application of Fick's Diffusion Law and Nernst-Planck Formulae for Electrical Potential—Consideration of Membrane Field Strength and Energetics of Permeation of Cations

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Electrolytic transport processes occurring across parchment supported membranes have been described by Nernst-Planck flux equation taking into account the membrane resistance R_m, membrane potential E_m *etc.* E_m values for various electrolytes display very interesting phenomena. In the case of 1: 1 electrolyte the E_m values are all positive, while in the case of (2: 1) and (3: 1) electrolytes surface charge reversal takes place. The diffusion rate sequence and selectivity of the membrane for different uni-, bi-, and tri-valent cations was found to be primarily dependent on the difference in the hydration energies of counter ions in the external solution. On the basis of Eisenman-Sherry theory the diffusion rate sequence of alkali metal cations point towards the weak field strength of the fixed charge groups. Various thermodynamic parameters, $\Delta H^{\neq}$, $\Delta F^{\neq}$, and $\Delta S^{\neq}$ were evaluated by applying the theory of absolute reaction rates to the diffusion process through parchment supported membranes. The values of $\Delta S^{\neq}$ were found to be negative, indicating that diffusion takes place with partial immobilization in the membrane phase. The relative partial immobility was found to increase with increase in the valence of the ions constituting the electrolyte. A formal relation between $\Delta H_{\text{hydration}}$, $\Delta F_{\text{hydration}}$, and $\Delta S_{\text{hydration}}$ of cations with the corresponding values of $\Delta H^{\neq}$, $\Delta F^{\neq}$, and $\Delta S^{\neq}$ for diffusion, was also found to exist for these membranes.

Transport processes occuring across membranes are of great interest for biologists, who use them as simple models for physiological membranes in order to understand the behavior of complex cell membranes in terms of established physico-chemical principles. It was demonstrated by Teorell[1)] that the gastric mucosal membrane, in some formal aspects at least, behaved exactly like parchment membrane. His findings, that electrolytic transport processes in stomach could be handled by something similar to Fick's diffusion law and that Nernst-Planck formulae for electrical potential were applicable, has encouraged us to proceed further with the studies of (a) the parchment supported membranes[2—9)] and (b) the asymmetric polymeric membranes[10—14)] which mimic some of the properties of nerve cells[15,16)] as models for biological system.

This paper deals with the studies of diffusion rate of biologically important electrolytes through parchment supported membranes. The results are discussed in the light of Eisenman-Sherry field strength model[17—20)] and the theory of absolute reaction rates.[21—23)]

Experimental

The parchment supported membranes of (i) silver (ii) cadmium hexacyanoferrate(II) and (iii) barium phosphate were prepared by the method of interaction described by Siddiqi *et al.*[2—9)] In order to precipitate these substances in the interstices of the parchment paper, 0.2 M solution of potassium hexacyanoferrate(II) was kept inside a glass tube to one end of which was tied the parchment paper. This was suspended for 72 h in a 0.2 M solution of silver nitrate or cadmium chloride (for hexacyanoferrate(II) membranes). The two solutions were interchanged later and kept for another 72 h. A similar procedure was adopted for the preparation of barium phosphate membrane by taking 0.5 M solutions of barium chloride and potassium di-hydrogen orthophosphate. The membranes thus prepared were washed with deionized water for removal of free electrolytes.

The apparatus and procedures used to measure membrane potential E_m, membrane resistance R_m, and electrolyte concentrations were described by siddiqi *et al.*[2)] The membrane was held between two half cells, each containing 125 ml of the electrolyte solution. Initially the concentrations C_1 and C_2 were 0.001 and 0.1 M, respectively. Each of the half cell was fitted with two platinized platinum electrodes firmly fixed to follow concentration changes and two anion reversible Ag–AgCl electrodes-one a disc type to pass a small d. c. current and the other a J-shaped wire electrode placed 1.7 cm apart from the membrane surface to measure membrane potential (Pye precision potentiometer No. 7568) and changes in membrane potential following current flow. The solutions in both the half cells were kept well stirred by magnetic stirrers. The whole cell assembly was immersed in a water thermostat maintained at 10, 15, 20, 25, and 30 °C (±0.1 °C).

Conductance changes on the dilute solution side was followed by means of the conductivity bridge (Cambridge Instrument Co. England No L-350140). The exact concentration of the solution at any given time was estimated from a calibration curve. The membrane resistance was determined by applying an external emf to the disc-type Ag–AgCl electrodes and measuring the change in potential across the membrane using J-type wire electrodes. The current passed through the membrane system was determined by measuring IR drop across a precision kilo-ohm resistor. The current was kept very low in order to minimize the ion transfer during the period (2—3 min) required for each resistance measurement. The direction of current flow was reversed in each successive measurement. The resistance measurements gave a value for the system electrolyte solution (R_e')-Membrane (R_m)-electrolyte solution (R_e''). In order to measure R_m directly, the wire electrodes should be placed strictly on the membrane surfaces. When this was done, resistance values were not reproducible This procedure was therefore abondoned in favor of the former and corrections for the electrolyte resistances R_e' and R_e'' were applied to derive a value for R_m. Since the geometry of the system (area=24.6 cm^2 and the distance at which wire electrode was placed from the membrane face=1.7 cm) and the specific conductance of the electrolyte solutions were known accurately (better than 0.5%), the sum ($R_e'+R_e''$) can be computed easily. Thus R_m, the membrane resistance only, can be derived as the difference between the measured total resistance and the sum of the calculated electrolyte resistances $(R_e'+R_e'')$. Although the membrane potential could be measured to a better accuracy than ±1%, the estimation of membrane resistance was accurate to ±3%.

Results and Discussion

The transport phenomena are often described by some extended form of the Nernst-Planck flux equation.[24] Evaluation of flows requires integration of these flux equations under suitable boundary conditions governing the behavior of the membrane system. Some time ago, Kittelberger[25] from the simple laws of electrolysis, developed the equation

$$\frac{dQ_+}{dt} = \frac{1}{Z_+FR_m}\left[\frac{RT}{Z_+F}\ln\frac{a_2}{a_1} - E_m\right] \times\left[\left(\frac{Z_+Z_-}{Z_++Z_-}\right)\left(\frac{E_m}{\frac{RT}{F}\ln\frac{a_2}{a_1}}\right)+\frac{Z_+}{Z_++Z_-}\right] \tag{1}$$

where Q_+ is the milli-equivalents of cations diffusing in time t s, Z_+, Z_- are the valencies of cation and anion, respectively, R_m is the resistance in ohm of the membrane, E_m is the membrane potential in millivolts, a_1 and a_2 are the activities of the two electrolyte solutions on either side of the membrane, R, T, and F have their usual meanings to describe the rate of flow of a charged species or electrolyte through a membrane.

$$\frac{Z_+Z_-}{Z_++Z_-}\,\frac{E_m}{\frac{RT}{F}\ln\frac{a_2}{a_1}} + \frac{Z_+}{Z_++Z_-} \tag{2}$$

is the cation transport number expressed in terms of observed membrane potential E_m. The term

$$\frac{RT}{Z_+F}\ln\frac{a_2}{a_1} - E_m \tag{3}$$

is the effective potential acting on the ion.

The emf measured across the membrane using the J-type Ag–AgCl electrodes is made up of two components, the electrode potential difference E_e due to the Ag–AgCl electrodes existing in the two chloride solutions of different activity a_1 and a_2, and the membrane potential E_m arising across the membrane due to flow of electrolyte through it. E_e is given by the equation

$$E_e = \frac{RT}{Z_-F}\ln\frac{C_2\nu_2}{C_1\nu_1} \tag{4}$$

where ν's are the activity coefficients of the electrolyte solutions. Since (E_e+E_m) is measured directly, E_m can be evaluated by substraction.

Changes in E_m and R_m with time are shown in Figs. 1 and 2 for various electrolytes diffusing through a cadmium hexacyanoferrate(II) membrane. At any given time, the membrane resistance R_m increases in the order; KCl, NaCl, LiCl, for electrolytes (1: 1), $CaCl_2$, $MgCl_2$, $BaCl_2$ for electrolytes (2: 1), and electrolyte (3: 1) $AlCl_3$ produces the highest value for R_m.

E_m values for the various electrolytes display a very interesting phenomenon. In the case of (1: 1) electrolytes, the values are all positive (dilute solution side C_1 taken as positive) indicating thereby that the membrane is cation selective. In the case of (2: 1) and (3: 1) electrolytes, E_m changes sign. This indicates that the membrane has become anion selective. The change in the selectivity character of the membrane is evidently due to adsorption of multivalent ions leading to a state where a net positive charge is left on the membrane surface taking it anion selective. Adsorption of Al^{3+} makes the membrane more anion selective than it is with the adsorption of other divalent cations. Such behavior seems to be observed with a number of other systems.[26–28]

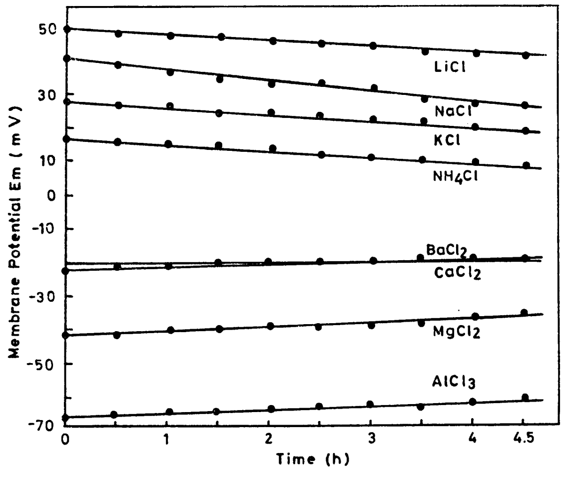

Fig. 1. Plots of membrane potential E_m against time for various electrolytes with cadmium hexacyanoferrate(II).

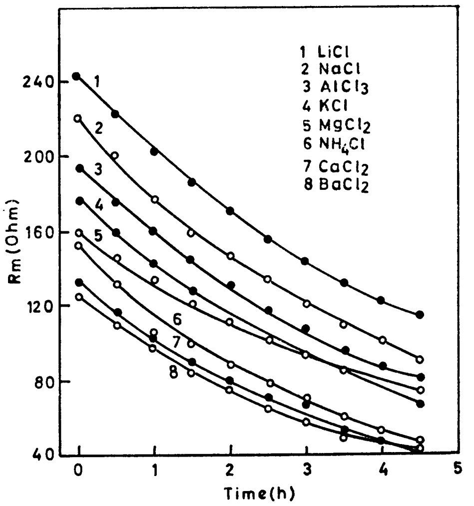

Fig. 2. Plots of R_m against time for various electrolytes with cadmium hexacyanoferrate(II).

The surface charge reversal occurred in every one of the membranes and electrolytes (2: 1) and (3: 1) and can be seen in the results given in Table 1 (a, b). E_m and R_m values are recorded.

With the help of Eq. 1, the rate at which various electrolytes diffuse through the membranes can be calculated. For electrolyte (1: 1), $(Z_+=Z_-=1)$, Eq. 1 becomes

$$\frac{dQ_+}{dt} = \frac{dQ_-}{dt} = \frac{dQ}{dt} = \frac{1}{2FR_m}\left[59.16\log\frac{C_2\nu_2}{C_1\nu_1} - E_m\right] \times\left[\frac{E_m}{59.16\log\frac{C_2\nu_2}{C_1\nu_1}}+1\right] \tag{5}$$

For electrolyte (2: 1), $(Z_+=2$ and $Z_-=1)$, it becomes

Table 1(a). Values of membrane potential E_m, membrane resistance R_m, and diffusion rate D_r at the end of 1/2 and 4 h periods at 25 °C[a)]

Membrane	Silver Hexacyanoferrate(II)						Cadmium hexacyanoferrate(II)					
Thickness	0.0381 cm						0.0279 cm					
Electrolyte	E_m (mV)		R_m (ohm)		D_r (μ mol/h)		E_m (mV)		R_m (ohm)		D_r (μ mol/h)	
	1/2 h	4 h	1/2 h	4 h	1/2 h	4 h	1/2 h	4 h	1/2 h	4 h	1/2 h	4 h
LiCl	77.5	61.4	260	143	3.7	6.3	48.5	43.0	223	123	7.0	9.2
NaCl	70.0	52.0	231	127	5.1	9.0	39.0	28.0	200	100	8.2	15.3
KCl	63.7	44.1	214	114	6.3	12.6	26.5	20.0	160	70	11.5	17.5
NH_4Cl	—	—	—	—	—	—	16.6	10.6	133	53	16.0	26.3
$BaCl_2$	−1.5	−20.9	117	55.5	5.0	8.5	−21.5	−17.3	118	50	6.3	11.5
$CaCl_2$	−11.6	−31.0	134	73.5	4.8	6.6	−21.6	−19.6	117	49	6.0	9.2
$MgCl_2$	−35.0	−40.4	181	108	4.0	5.0	−41.9	−35.0	147	79	5.0	6.3
$AlCl_3$	−67.4	−75.0	226	140	0.8	0.5	−65.6	−61.5	177	87	1.5	2.8

a) Area of membrane=24.6 cm².

Table 1(b). Values of membrane potential E_m, membrane resistance R_m, and diffusion rate D_r at the end of 1/2 and 3 h periods at 25 °C[a)]

Membrane	Barium phosphate					
Thickness	0.03612 cm					
Electrolyte	E_m (mV)		R_m (ohm)		D_r (μ mol/h)	
	1/2 h	3 h	1/2 h	3 h	1/2 h	3 h
KCl	12.72	7.10	155.0	55.0	10.483	22.70
NaCl	4.53	−0.73	180.2	84.0	7.894	15.624
LiCl	3.12	0.60	221.1	136.0	7.107	9.493

a) Area of membrane=24.6 cm².

$$\frac{dQ_+}{dt} = \frac{1}{2}\frac{dQ_-}{dt} = \frac{dQ}{dt} = \frac{1}{3FR_m}\left[29.58 \log \frac{C_2v_2}{C_1v_1} - E_m\right] \times \left[\frac{E_m}{59.16 \log \frac{C_2v_2}{C_1v_1}} + 1\right] \tag{6}$$

For electrolyte (3: 1), ($Z_+=3$ and $Z_-=1$), it becomes

$$\frac{dQ_+}{dt} = \frac{1}{3}\frac{dQ_-}{dt} = \frac{dQ}{dt} = \frac{1}{4FR_m}\left[19.72 \log \frac{C_2v_2}{C_1v_1} - E_m\right] \times \left[\frac{E_m}{59.16 \log \frac{C_2v_2}{C_1v_1}} + 1\right] \tag{7}$$

The electrolyte fluxes dQ/dt *i.e.* D_r calculated from Eqs. 5—7 for various electrolytes at 25 °C are given in Table 1 for all the three membranes. The reproducibility of the results were within ±3% at a certain temperature. The changes in R_m, E_m, and D_r with time for cadmium hexacyanoferrate(II) membrane are shown in Figs. 1—3, while comparative values for various cations are given in Fig. 3a.

The diffusion rate derived from the electrometrically or conductometrically determined changes in the salt concentration of the test solution C_1 is called "observed diffusion rate," while the values computed from the measured concentration potential and electrolytic resistance of the membrane *i.e.* from Eqs. 5—7 is designated the "computed" diffusion rate. The "computed" and "observed" diffusion rates of KCl, NaCl, LiCl for barium phosphate membrane are shown in Fig. 4a. For

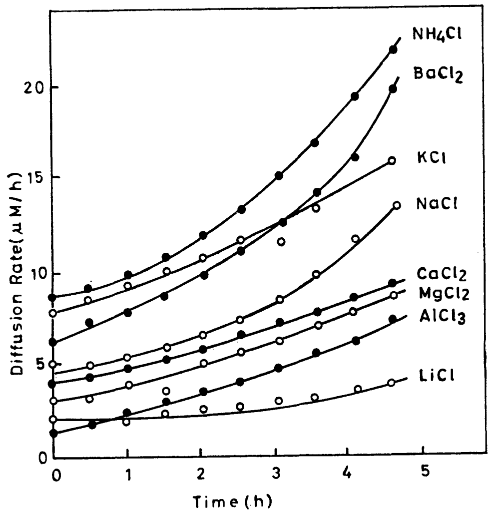

Fig. 3. Plots of diffusion rate *vs.* time through cadmium hexacyanoferrate(II).

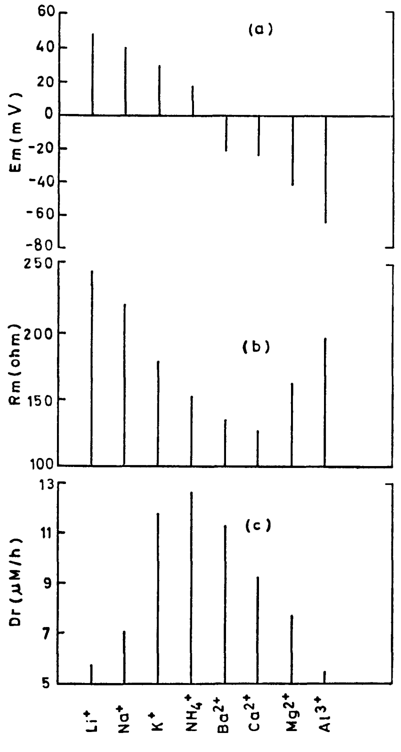

Fig. 3a. Plots of E_m, R_m, and D_r against the various electrolytes for cadmium hexacyanoferrate(II).

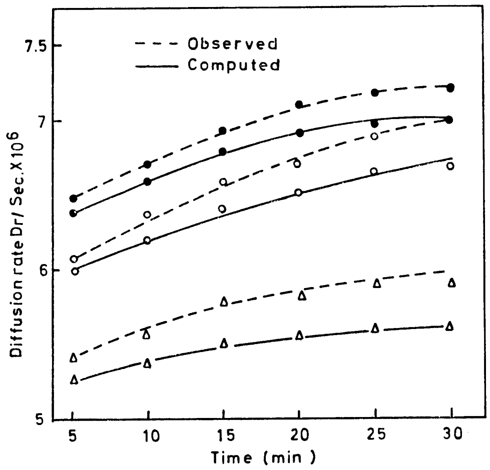

Fig. 4a. Plots of observed and computed diffusion rate against time for ●: KCl, ○: NaCl, and △: LiCl with barium phosphate membrane.

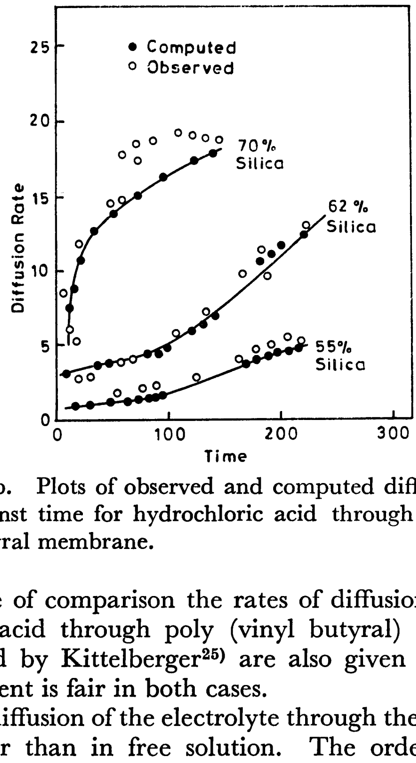

Fig. 4b. Plots of observed and computed diffusion rate against time for hydrochloric acid through polyvinyl butyral membrane.

the sake of comparison the rates of diffusion of hydrochloric acid through poly (vinyl butyral) membranes obtained by Kittelberger25) are also given in Fig. 4b. Agreement is fair in both cases.

The diffusion of the electrolyte through the membrane is slower than in free solution. The order does not remain the same due to various reasons; (a) only a part of the frame work is available for free diffusion, (b) the diffusion paths in the membrane phase are more tortuous and therefore longer (*i.e.* the tortuousity factor), (c) the large hydrated ions in the narrow mesh region of the membrane might be impeded in their mobility by the frame work and (d) the interaction of the diffusing species with the fixed groups on the membrane matrix. Parchment paper, except for the presence of some stray and end carboxyl groups, contains very few fixed groups. Deposition of inorganic precipitate gives rise to a net negative charge on the membrane surface in the case of electrolyte (1: 1) leading to the type of ionic distribution associated with the electrical double layer. However, use of electrolyte (2: 1) or (3: 1) leaves a net positive charge on the membrane and results in the formation of the electrical double layer. The system is considered as having charged capillary structures or gels which can be judged in the light of classical fixed charge theory of Teorell,29) Meyer and Sievers,30) Sollner,31) Gregor,32) and Schmid.33,34) Flow of electrolyte by diffusion because of the presence of a net charge (*—ve* or *+ve*) on the membrane gives rise to the membrane potential as opposed to the liquid junction potential ordinarily observed under similar conditions in the absence of the membrane, which regulates the flow of electrolyte by increasing the speed of slow moving ion and by decreasing the speed of the faster moving ion. The regulated rate of flow (*i.e.* diffusion) measured for different electrolytes through the investigated membranes follow the sequence: $\mathrm{NH_4^+}>\mathrm{K^+}>\mathrm{Na^+}>\mathrm{Li^+}$ and $\mathrm{Ba^{2+}}>\mathrm{Ca^{2+}}>\mathrm{Mg^{2+}}>\mathrm{Al^{3+}}$.

Depending on the size and electrical charge pattern of a pore, it may either admit or repel a solute particle. This is the basis of ion selectivity. Mullins35) proposed that the hydration of the materials of the pores themselves may provide a favorable water environment for particular ions or molecules, so that they slip into the pores away from their previous water molecules. This could result in selection of a particular size with discrimination against both smaller and larger hydrated ions. In order to obtain a quantitative relation between the ease of penetration and the ion size, it is necessary to know the electrostatic force which acts between the ions and the material of the membranes, since this force provides energy to displace water of hydration. Eisenman *et al.*17–19) pointed out that the order of the ease of penetration of cations depends on the energy available from the ion-fixed charge interaction. From a simplified model, in which field strength was taken as a controlling variable, the Coulomb energies of interaction of alkali cations with the charged sites were compared with the free energy of hydration of cations. A simplified theory of selectivity for four alkaline earths ($\mathrm{Mg^{2+}}$, $\mathrm{Ca^{2+}}$, $\mathrm{Sr^{2+}}$, and $\mathrm{Ba^{2+}}$) in a cation exchange membrane has been worked out by Sherry.20) Specificity is determined by the difference between the free energy of hydration of

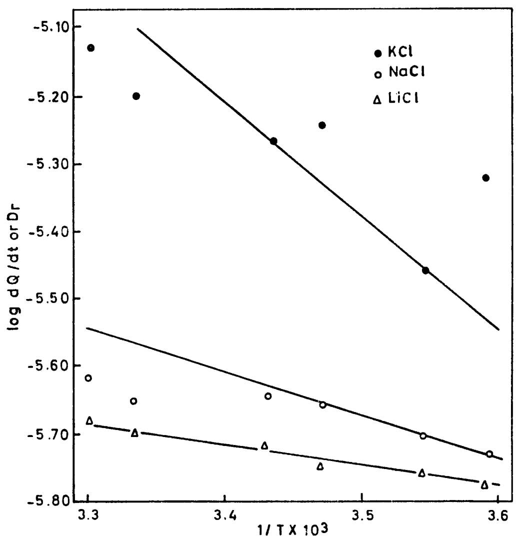

Fig. 5. Plots of log D_r *vs.* $1/T$ for different electrolytes with barium phosphate membrane.

Table 2(a). Experimental activation energy E_a and other thermodynamic parameters calculated from transition state theory of rate processes for various electrolytes diffusion, through membrane (Temperature=25 °C)

Membrane	Silver hexacyanoferrate(II)				Cadmium hexacyanoferrate(II)			
Electrolyte	E_a kcal mol^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta F^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ e.u.	E_a kcal mol^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta F^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ e.u.
LiCl	5.53	4.94	8.80	−13.0	6.36	5.77	8.79	−10.1
NaCl	5.97	5.38	8.85	−11.6	7.15	6.37	8.68	− 7.9
KCl	6.26	5.67	8.81	−10.5	7.50	6.95	8.58	− 5.8
NH_4Cl	—	—	—	—	7.65	7.06	8.56	− 5.1
$BaCl_2$	4.24	3.65	8.85	−17.5	4.61	4.02	8.95	−16.5
$CaCl_2$	3.68	3.09	9.90	−19.8	4.24	3.65	9.11	−18.3
$MgCl_2$	3.96	3.37	9.13	−19.4	4.61	4.02	9.25	−17.6
$AlCl_3$	3.41	2.82	9.72	−23.1	3.32	2.73	9.86	−23.9

Table 2(b). Experimental activation energy E_a and other thermodynamic parameters calculated from transition state theory of rate processes for various electrolytes diffusion, through membrane (Temperature=25 °C)

Membrane	Barium phosphate			
Electrolyte	E_a kcal mol^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta F^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ e.u.
KCl	5.45	4.84	7.83	−10
NaCl	4.21	3.61	8.08	−15
LiCl	3.09	2.50	9.06	−22

alkaline earth cations and their Coulomb energies of interaction with the negatively charged sites. On the basis of Eisenman-Sherry theory,[17–20)] the diffusion rate sequence obtained with the investigated membranes point towards the weak field strength of charged groups.

The theory of absolute reaction rates[21–23)] has been applied to diffusion processes in membranes by several investigators.[36–39)] According to Laidler *et al.*[22–23)] the integral diffusion coefficient $\bar{D}$ is given by the expression

$$\bar{D} = Ae^{-E_a/RT} \tag{8}$$

where E_a is the observed activation energy for diffusion and A is the frequency factor. Thus, if log D is plotted against $1/T$, the slope gives (Fig. 5) the value of energy of activation for the diffusion process. These values of E_a were determined for a number of electrolytes and with all the three membranes, and are given in Tables 2 (a, b).

According to Zwolinski *et al.*,[21)] we have

$$\bar{D} = \lambda^2\left(\frac{KT}{h}\right)\exp\,(\Delta S^{\ddagger}/R)\exp\left(\frac{-\Delta H^{\ddagger}}{RT}\right) \tag{9}$$

where λ is the distance between successive equilibrium positions of diffusing species, $\Delta S^{\ddagger}$ the entropy of activation, $\Delta H^{\ddagger}$ the enthalpy of activation, k, h, R, and T having their usual meanings.

The Eyring enthalpy of activation $\Delta H^{\ddagger}$ is calculated from the activation energy E_a (previously determined) by means of the relation

$$\Delta H^{\ddagger} = E_a - RT \tag{10}$$

Assuming λ to be equal to 3 Å for different electrolytes (values 1—5 Å for λ have been used by different investigators) and substituting the value of diffusion coefficient $\bar{D}$, the value of $\Delta S^{\ddagger}$ has been calculated. The free energy of activation $\Delta F^{\ddagger}$ is then calculated by the Gibbs-Helmholtz equation

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{11}$$

The values so derived for the different thermodynamic parameters are given in Tables 2 (a, b).

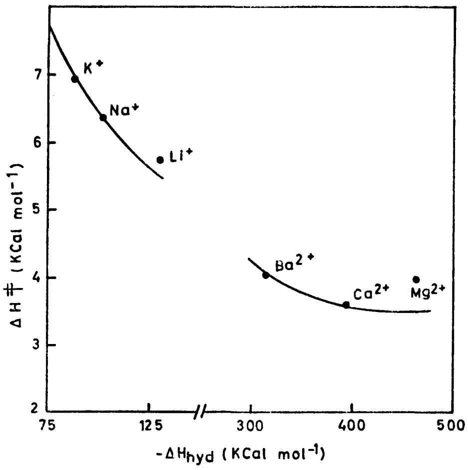

Fig. 6a. Plots of $\Delta H^{\ddagger}$ for the diffusion of various electrolytes (at 25 °C) against $-\Delta H_{hyd}$ for the respective cations through cadmium hexacyanoferrate(II).

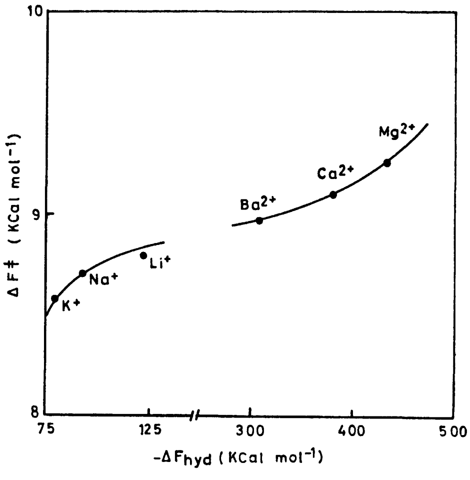

Fig. 6b. Plots of $\Delta F^{\ddagger}$ for the diffusion of various electrolytes (at 25 °C) against $-\Delta F_{hyd}$ for the respective cations through cadmium hexacyanoferrate(II).

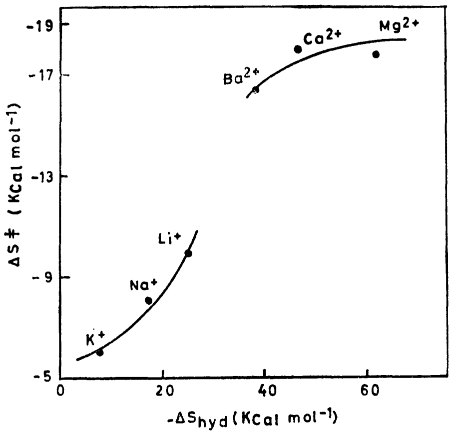

Fig. 6c. Plots of $\Delta S^{\ddagger}$ for the diffusion of various electrolytes (at 25 °C) against $-\Delta S_{\mathrm{hyd}}$ for the respective cations through cadmium hexacyanoferrate(II).

The results indicate that electrolyte permeation gives rise to negative values of $\Delta S^{\ddagger}$. The values of $\Delta S^{\ddagger}$ for all the three membranes show a similar behavior for different electrolytes. With increase in valence of the individual ion, the decrease in the values of $\Delta S^{\ddagger}$ is enhanced. It is believed that the membrane and not the solution-membrane interface controls the electrolyte diffusion process. The negative values of $\Delta S^{\ddagger}$ as suggested by Schular *et al.*[23] indicate electrolyte diffusion with partial immobilization in the membrane, the relative partial immobility increasing with increase in the valence of ions constituting the electrolyte. In Fig. 6 (a, b, c) the individual ionic contribution to the properties of aqueous ions given by Noyes[40] namely $\Delta H_{\mathrm{hydration}}$, $\Delta F_{\mathrm{hydration}}$, and $\Delta S_{\mathrm{hydration}}$, of Li^+, Na^+, K^+, as well as those of Ba^{2+}, Ca^{2+}, and Mg^{2+} are plotted against the corresponding $\Delta H^{\ddagger}$, $\Delta F^{\ddagger}$, and $\Delta S^{\ddagger}$ values for diffusion through the membrane. It is found that at least some formal relationship exists between these thermodynamic parameters.

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