Int. J. Chem. Sci.: 10(2), 2012, 1043-1055
ISSN 0972-768X
www.sadgurupublications.com

EVALUATION OF THERMODYNAMIC ACTIVATION PARAMETERS OF COBALT ORTHOVANADATE MEMBRANE

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ABSTRACT

In the present work, the preparation of parchment supported cobalt orthovanadate membrane has been described. The ion transport through the membrane has been computed using the Kittelberger's equation based on the simple laws of electrolysis. The assembly used provides the data for various membrane parameters like membrane resistance, membrane potential and the diffusion rate of ions within a very short period, i.e. within two – three minutes, with reasonable accuracy. By applying the theory of absolute reaction rate, various thermodynamic parameters, namely, enthalpy of activation $\Delta H^{\neq}$, energy of activation $\Delta F^{\neq}$, and entropy of activation $\Delta S^{\neq}$ were evaluated. The $\Delta S^{\neq}$ values were found to be negative, indicating that diffusion takes place with partial immobilization in the membrane phase. A formal relation between $\Delta F_{hydration}$, $\Delta H_{hydration}$ and $\Delta S_{hydration}$ of cations with corresponding values of $\Delta F^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for diffusion was also worked out.

Key words: Membrane potential, Ionic transport, Thermodynamic parameters.

INTRODUCTION

We have been engaged in the studies of (a) parchment supported, (b) polystyrene - based ion exchange membranes[1–8], which can serve as models for biological systems. 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[9–18] 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. In this article the

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preparation of parchment supported cobalt orthovanadate membrane has been described. The following aspects of parchment - supported membranes were dealt: application of Nernst – Planck flux equations and Fick's diffusion law[19] and evaluation of various thermodynamic activation parameters.

EXPERIMENTAL

Parchment supported cobalt orthovanadate membrane was prepared by the method of interaction. 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 cobalt chloride solution. This was suspended for 72 hours in a 0.2 M sodium orthovanadate solution at room temperature. The two solutions were interchanged and kept for another 72 hours. In this way fine deposition of cobalt orthovanadate 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 then cut into a circular disc form and was clamped between two half cells of an electrochemical cell. Each of the half cell was fitted with a conductivity cell (λ_1 and λ_2) to follow concentration changes and two anion reversible Ag-AgCl electrodes – one a disc type (D_1 and D_2) to pass a small d.c. current and the other a J shaped wire electrode (J_1 and J_2) placed very near the membrane surface to measure membrane potential and also to follow changes in potential due to the external applied voltage. The capacity of each of the half cells holding the membrane was about 130 mL. Initially the electrolyte concentrations C_1 and C_2 on the two sides of membrane were 0.001 M and 0.1 M respectively. The whole cell assembly was immersed in a water thermostat maintained at 10, 15, 20, 25, 30 ± 0.1°C. The solutions were vigorously stirred by a pair of magnetic stirrers.

Exactly known weights or volumes of two test solutions were introduced (say at zero time). The conductivity cells were connected to the conductance bridges (Cambridge Instrument Co. England, No. 350140) to follow conductance changes with time. No appreciable change in conductance was noted within 3.5 hr period on the C_2 side (0.1 M) and so we have assumed this concentration to be practically constant and followed only the conductance changes on the C_1 side. The exact concentration of this solution was determined from a calibration curve where conductance was plotted against concentration. Another set of calibration curves were needed to obtain concentration potential E_C^+ from the plots of emf against log fc according to the equation.

$$E_C^+ = RT / Z_+ \ln fc \qquad \ldots(1)$$

These were obtained by using a pair of saturated calomel and Ag-AgCl electrodes in the test solutions. For all the electrolytes under investigation E_{C+} was taken as the difference between emf values of the dilute and the concentrated solutions.

Membrane resistance R_m, and membrane potential E_m were determined by measuring potential (using pye precision vernier potentiometer No. 7568) across J_1 and J_2 electrodes with and without applying an external emf to the disc electrodes. The potential in absence of external applied voltage was equal to the algebraic sum of the concentration potential Ee- and the membrane potential E_m (i.e. E_e- + E_m). The concentration potential difference E_e- was calculated using equation –

$$E_e\text{-} = \frac{RT}{ZF} \ln \frac{C_2f_2}{C_1F_1} \quad ...(2)$$

From the measured concentration of the electrolytes on the two sides of the membrane and E_m was obtained by subtraction. The change in potential due to applied voltage was taken as IR_m. The current I 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 measurements. The direction of current flow was reversed in each successive measurement. The error in the membrane potential measurements was within ± 1%, whereas the estimation of membrane resistance was accurate upto 98%. The various salt solutions (chlorides of K^+, Na^+, Li^+, Ca^{2+}, Ba^{2+}, Mg^{2+} and Al^{3+}) were prepared from analytical grade (BDH) reagents using deionized water.

RESULTS AND DISCUSSION

When an ionic gradient is maintained using different concentrations of an electrolyte on either of the membrane, diffusion of electrolyte from the region of high concentration takes place. There will be flow of water in the opposition direction. Besides, an electric field due to the differences in the ionic mobilities is established across the membrane. If the membrane contains a large number of fixed groups, say a negative charge, the potential gradient will be many times larger than the liquid junction potential which is normally observed when the same two solutions are brought together with or without "uncharged" membrane in between. These transport phenomena are often described by some extended form of Nernst-Planck flux equation[19]. Evaluation of flow requires integration of these flux equations under suitable boundary conditions governing the behaviour of the membrane-electrolyte system. Apart from these, due to the complexity of membrane structures and its functions, various mathematically rigorous equations based on numerous theoretical descriptions have been derived and their simplifications made. The diversity in the theoretical forms for transport phenomena, which results from simplifications made by various authors, is a particular hazard to workers in this field.

Sometimes ago Kittleberger[20] developed the following equation for the diffusion rate of ions through a barrier using the simple laws of electrolysis and utilized it for the investigation of transport parameters in polyvinylbutyral membrane.

$$\frac{dQ_+}{dt} + \frac{1}{z+FR_m}\left[\frac{RT}{z_+F}\ln\frac{a_2}{a_1} - E_m\right]\left[\left(\frac{Z_-}{z_+ + z_-}\right)\left\{\frac{E_m}{\frac{RT}{F}\ln\frac{a_2}{a_1}}\right\}\left(\frac{Z_+}{z_+ + z_-}\right)\right] \quad \ldots(3)$$

Where Q_+ is the milliequivalent of cation diffusing in time t sec, z_+ and z_- are the cationic and anionic valencies 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 solutions on either side of the membrane, R, T and F have their usual significance.

The term

$$\frac{Z_-}{z_+ + z_-}\;\frac{E_m}{\frac{RT}{F}\ln\frac{a_2}{a_1}} + \frac{Z_+}{z_+ + z_-} \quad \ldots(4)$$

is the cation transport number, expressed in terms of E_m with solution activities a_1 and a_2 present on either side of the membrane and the term

$$\frac{RT}{z_+F}\ln\frac{a_2}{a_1} - E_m \quad \ldots(5)$$

is the effective potential acting on the cation.

Equation 3 was used to calculate the diffusion rate of ions through membranes. For 1 : 1 electrolytes ($z_+ = z_- = 1$), equation 3 becomes

$$\frac{dQ_+}{dt} = \frac{dQ_-}{dt} = \frac{dQ_-}{dt} = \frac{1}{2FR_m}\left[59.16\ \log\frac{C_2f_2}{C_1f_1} - E_m\right]\left[\frac{E_m}{59.16\log\frac{C_2f_2}{C_1f_1}} + 1\right] \quad \ldots(6)$$

For 2 : 1 electrolyte, ($z_+ = 2$, $z_- = 1$), equation 3 becomes

$$\frac{dQ_+}{dt} = 1/2\frac{dQ_-}{dt} = \frac{dQ_-}{dt} = \frac{1}{2FR_m}\left[29.16\ \log\frac{C_2f_2}{C_1f_1} - E_m\right]\left[\frac{E_m}{59.16\log\frac{C_2f_2}{C_1f_1}} + 1\right] \quad \ldots(7)$$

The rates at which various electrolytes diffuse through the membrane were calculated at different temperatures from equation 3. The calculated values of diffusion rate (dQ / dt) or D_r in mM / s at 25 ± 0.1°C are given in Table 1. The changes in R_m and E_m and electrolyte flux (dQ / dt) or D_r, through cobalt orthovanadate membrane are shown in Fig. 1.

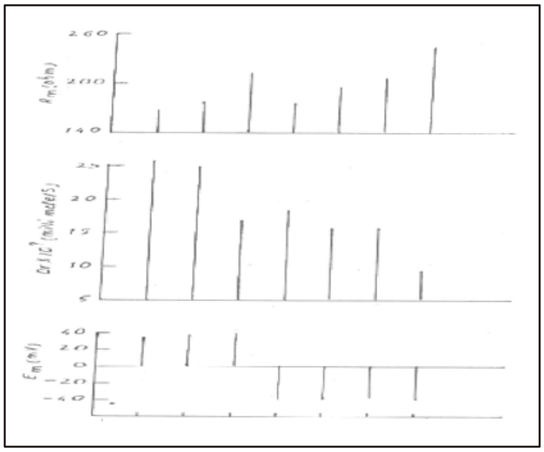

Fig. 1: K^+, Na^+, Li^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+} Plots of E_m, R_m and D_r against various electrolytes across cobalt or thoranadate membrane ac 25°C

This may be ascribed to be due to the increase in the ion association with the membrane exchange groups. This is in agreement with the findings of Subramanyam and Lakshminarayanaiah[21] and Gregor and co-workers[22] for the AMF C-103 membrane, and those of Beg and coworkers[9–18] with parchment supported inorganic precipitate membranes[9,12,14].

The values of E_m decrease with time though almost to a negligible extent, for various diffusing electrolytes through parchment supported cobalt orthovanadate membrane. The change in E_m may be due to the small changes produced in the concentration of electrolyte solutions during the diffusion time. The membrane potential sequence for alkali metal ions was Li^+, Na^+, K^+ and for multivalent cations it was Al^{3+}, Ba^{2+}, Ca^{2+}, Mg^{2+}. This sequence of membrane potential point towards the fact that multivalent ions are more strongly adsorbed on the membrane skeleton than univalent ions and that aluminium being most strongly adsorbed[9].

Table 1: Values of Diffusion rate D_r of various electrolytes at the end of 2 hr period at 25 ± 0.1°C through parchment supported Cobalt Orthovanadate membrane

Electrolytes	$D_r \times 10^7$ (mM / S)
KCl	25.8
NaCl	24.6
LiCl	16.8
$BaCl_2$	18.4
$CaCl_2$	15.6
$MgCl_2$	15.5
$AlCl_3$	9.5

The values of diffusion rate dQ/dt for various cations were calculated from the predetermined values of membrane potential E_m and membrane resistance R_m using equations 6 and 7. The diffusion of electrolytes through the membrane is slower than in free solution. This may be due to various reasons namely, (a) only a part of framework is available for free diffusion, (b) the diffusion paths in the membrane phase are more torturous and therefore longer, (c) the large hydrated ions in the narrow mesh region of the membrane be impeded in their mobility by the framework and (d) the interaction of the diffusing species with the fixed groups on the membrane matrix. The diffusion rate sequence of cations through the membrane was K^+, Na^+, Li^+ and Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}. This diffusion rate sequence on the basis of Eisenman – Sherry model of membrane selectivity[23–25] point towards the weak field strength of charge groups attached to the membrane skeleton.

Parchment paper, except for the presence of some stray 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 dilute solutions of electrolytes (1 : 1) leading to the type of ionic distribution associated with the electrical double layer. However, use of concentrated electrolytes (1 : 1), (2 : 1), or (3 : 1) leaves a net positive charge on the membrane surface due to the preferential adsorption of cations. This type of charge reversal is not peculiar to these systems. Flow of electrolyte by diffusion because of the presence of a net charge (- ve or + ve) on the membrane gives rise to 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 ions. The regulated rate of flow for various electrolytes through the investigated membranes follow the sequence K^+, Na^+, Li^+ and Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}.

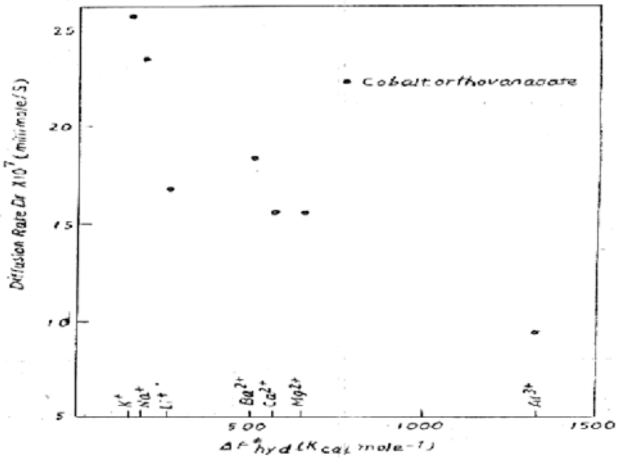

Fig. 2: Diffusion rate at 25°C for various electrolytes (chloride) through cobalt orthovanadate membrane plotted against free energy (F) of hydration of cations

Membrane porosity in relation to the size of the species (hydrated) flowing through the membrane seems to determine the above sequence. Although the size of the hydrated electrolytes are not known with certainty, there are few tabulations[26,27] of the number of moles of water associated with some electrolytes. However, in Fig. 2 a plot of diffusion rate dQ / dt of different electrolytes (chlorides) against free energy of hydration of cations is given for the membrane. It is seen that diffusion rate decreases with increasing hydration energy, that is, greater size due to increase in hydration. This points to the fact that the electrolyte is diffusing along the pores or channel of dimension adequate enough to allow the substance to penetrate the membrane. The state of hydration of the penetrating electrolyte may be considered to exist in a dynamic condition so that at higher temperatures considerably higher fraction f of the total number of a given kind would possess excess energy E according to the Boltzmann distribution $f = e^{-E/RT}$ (F is the gas constant). Under these circumstances, those ionic species which have lost sufficient water of hydration to be smaller than the size of the pore would enter the membrane. In this way the permeability would increase with increase in temperature subject, however, to the provison that the membrane has undergone no irreversible change in its structure. That no such structural change is involved is evident in Fig. 3. The slope of these lines which is equal to $E_a/2.303$ R gives the activation energy E_a required for diffusion process. The values of E_a so derived are given in Table 2.

The diffusion rate dQ / dt (millimole /h) is related to diffusion coefficient--

D (cm / sec) by the relation

$$D = dQ / dt \times 10^{-6} / 3.6\, A\, \Delta C \qquad \ldots(8)$$

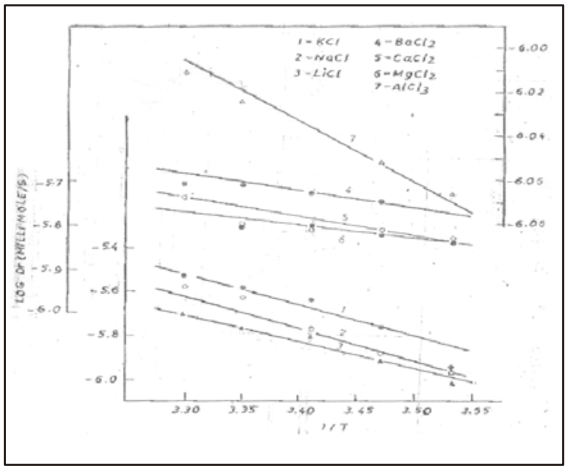

Fig. 3: Plots of log Dr against I/T for various electrolytes with cobalt orthoranadate membrane

Where A is the membrane area (24.6 cm^2) and ΔC is the difference in the electrolyte concentration exist across the membrane. Since areas of membrane and concentration difference of electrolytes are constant, therefore diffusion coefficient is proportional to dQ/dt and thus the slope of linear plots of log D vs. (1/T) and of log dQ/dt vs. (1/T) will be same.

The theory of absolute reaction rate[28] has been applied to diffusion processes in membrane by several investigators[28–32]. According to Zwolinski et al.,[28] we have

$$D = \lambda^2 (KT / dh) \exp - \Delta F^{\neq} / RT \qquad \ldots(9)$$

Where K is Boltzmann constant, d is membrane thickness, h is Planck constant, and λ is average distance between equilibrium positions in the process of diffusion. $\Delta F^{\neq}$ is the free energy of activation for diffusion and is related to enthalpy $\Delta H^{\neq}$, and entropy of activation $\Delta S^{\neq}$ of diffusion by the Gibbs-Helmholtz equation

$$\Delta F^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad \ldots(10)$$

$\Delta H^{\neq}$ is related to Arrhenius energy of activation E_a by the equation

$$\Delta H^{\neq} = E_a + RT \qquad \ldots(11)$$

As the values of the membrane thickness d, the universal constant h, and the gas constant R are known, the values of $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta F^{\neq}$ can be calculated provided the value of λ is known. Different investigators[28–31,33] have used value of λ ranging from 1–5 Å. In this work, a value of 1Å has been used in the calculations, and the values of different thermodynamic parameters, so derived for the membrane and various electrolytes are given in Table 2.

Table 2: Experimental activation energy E_a and other thermodynamic parameters calculated from transition state theory of rate process for cobalt orthovanadate membrane at 25 ± 0.1°C

Electrolytes	**E_a (Kcal mole^{-1})**	**$\Delta H^{\neq}$ (Kcal mole^{-1})**	**$\Delta F^{\neq}$ (Kcal mole^{-1})**	**$\Delta S^{\neq}$ (e.u)**
KCl	7.08	6.49	9.91	-11.48
NaCl	6.34	5.74	9.96	- 14.13
LiCl	5.49	4.89	10.17	- 17.72
$CaCl_2$	2.47	1.88	10.20	- 27.92
$BaCl_2$	2.28	1.69	10.11	- 28.26
$MgCl_2$	1.72	1.13	10.21	- 30.47
$AlCl_3$	1.69	1.09	10.50	- 33.56

The values of $\Delta S^{\neq}$ are either positive or negative for membranes. There are a few values which are close to zero and correspond to liquid systems. According to Erying and coworkers[28,29], the values of $\Delta S^{\neq}$ indicate the mechanism of flow; large positive $\Delta S^{\neq}$ is interpreted to reflect breakage of bonds, while low values indicate that permeation has taken place without breaking bonds. The negative $\Delta S^{\neq}$ values are considered to indicate either formation of covalent bond between the permeating species and the membrane material or that the permeation through the membrane may not be the rate determining step. On the contrary, Barrer[31,34,35] has developed the concept of "Zone activation" and applied it to the permeation of gases through polymer membranes. According to this zone hypothesis, a high $\Delta S^{\neq}$, which has been correlated with high energy of activation for diffusion, means either the existence of a large zone of activation or the reversible loosening of more chain segments of the membrane. A low $\Delta S^{\neq}$, then means either a small zone of activation or no loosening of the membrane structure on permeation. In view of these differences in the interpretation of $\Delta S^{\neq}$, Shuller et al.,[30] who found negative $\Delta S^{\neq}$ values for sugar permeation through collodion membranes, have stated that "it would probably be correct to interpret the small negative values of $\Delta S^{\neq}$ mechanically as interstitial permeation of the membrane (minimum chain loosening) with partial immobilization in the membrane phase (small zone of disorder)". On the other hand, Tien and Ting[33] who found negative $\Delta S^{\neq}$ values for the permeation of water through very thin (50 Å thickness) bilayer membranes, stressed the possibility that the membrane may not be the rate determining step. Based on additional experimental data, they came to the conclusion that the solution membrane interface was the rate-limiting step for permeation. The results reported here (Table 2) indicate that electrolyte permeation gives rise to negative values for $\Delta S^{\neq}$. It is in general found that as the valence of the individual ion is increased, the decrease in the value of $\Delta S^{\neq}$ is enhanced. Since the membrane used in this study is fairly thick and that the electrical double layer changes the characteristics in contact with different electrolytes, it is believed that the membrane along with the solution-membrane-interface controlled the electrolyte permeation process. The negative values of $\Delta S^{\neq}$, therefore, as suggested by Shuller et al.,[30] indicate electrolyte permeation with partial immobilization in the membrane, the partial immobility increases in a relative manner with increase in the valence of the ions constituting the electrolyte.

In Figs. 4-6 the individual ionic distribution to the property of aqueous ions, namely $\Delta F_{hydration}$, $\Delta H_{hydration}$, $\Delta S_{hydration}$ of Li^{+}, Na^{+}, K^{+} as well as those of Ba^{2+}, Ca^{2+} and Mg^{2+} are plotted against the corresponding $\Delta F^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ values for diffusion through the membrane[36-39]. It is found that at least some formal relationship exists between these thermodynamic parameters, which consequently support the "activation barrier" kinetic approach for the investigation of the system under study.

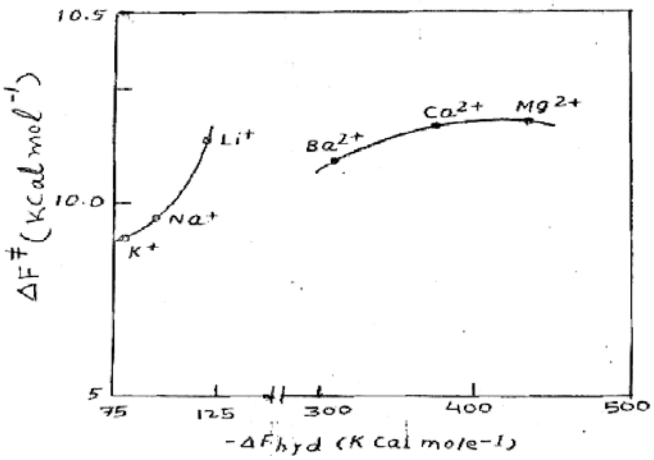

Fig. 4: Plots of $\Delta F^{\neq}$ (Kcal/mol) for the diffusion of various electrolytes (at 25°C) against – $\Delta F_{hyd.}$ (Kcal/mol) for Respective castions through cobalt orthovanadate membrane

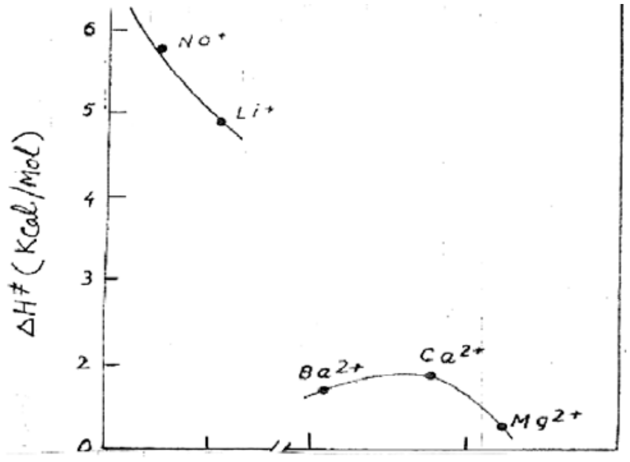

Fig. 5: Plots of $\Delta H^{\neq}$ (Kcal/mol) for the diffusion of various electrolytes (at 25°C) against – $\Delta H_{hyd.}$ (Kcal/mol) for Respective castions through cobalt orthovanadate membrane

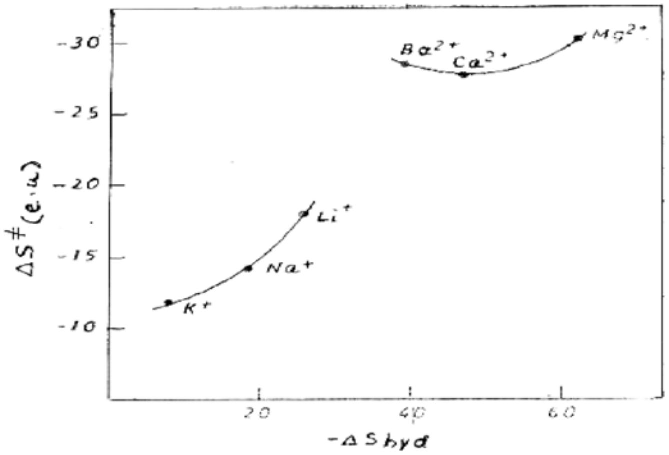

Fig. 6: Plots of ΔS (e.u.) for the diffusion of various electrolytes (at 25°C) against – $\Delta S_{hyd.}$ (Kcal/mol) for Respective castions through cobalt orthovanadate membrane

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Accepted : 04.03.2012