TECHNICAL REPORT

STUDIES ON THERMODYNAMIC PARAMETERS OF DIFFUSION PROCESS THROUGH ALUMINIUM FERROCYANIDE MEMBRANE

Sat Paul Arora and D. K. Rastogi*

Chemical Laboratory, Mukand Lal National College, Yamuna Nagar

*(*Lecturer in Chemistry, Meerut College, Meerut)*

(Received Oct. 1977; accepted Dec. 1977)

Permeability measurements of Various electrolytes through Polystyrene-supported Aluminium Ferrocyanide membrane have been carried out. The diffusion rates are temperature dependent and increase with temperature. The activation energy values for different electrolytes through membranes are higher than those for free diffusion. The thermodynamic parameters ($\triangle F$ and $-\triangle S$) increase regularly with the the size of anions as well as the cations. However no regular trend in case of $\triangle H$ is observed.

The transport of charged or uncharged particles across different types of membranes is really a complex phenomenon. Various theories [1–14] have been put forward to explain the diffusion process through the membranes from time to time. Recently Malik et al [5–7] have done a lot of work on metal hydroxides and metal ferrocyanides parchment-supported membranes.

The present communication deals with the studies on the effect of temperature on the permeability measurements of various electrolytes on the polystyrene supported Aluminium Ferrocyanide membrane and therefrom the activation energy of the diffusion process has been calculated. Thermodynamic parameters of the diffusion process such as change in enthalpy, free energy and entropy have also been determined.

Experimental Methods

Preparation of Membrane: The membrane was prepared by heating 1.5 gms. homogenised mixture of Aluminium Ferrocyanide gel and polystyrene powder (4:1) in a specimen mount press at 115°C under pressure[8].

Premeability Measurements: Permeability measurements were carried out by Willis constant flow methods[9]. The hydrostatic pressure on each side of the membrane was kept equal by adjusting the rate of flow of electrolyte and conductivity of water across the mem brane. The analysis of effluent coming out of the lower half cell was made conductometrically. Knowing the rate of flow and concentration of effluent coming out of the lower half cell, (from concentration conductance curves) the permeability in millimoles per hour at different temperatures (20,25,30,35, and 40°C) was determined.

The diffusion rates are found to be highly dependent on temperature showing an increase with temperature. The plots between diffusion values, log $(P \times 10^3)$ Vs $\frac{1}{T} \times 10^3$ give in all the cases straight lines. The E_a values, (Table 1) lie between 6.525 to 9.089 KCal per mole. The values of activation energy calculated in the percent study are much higher than those for free diffusion of electrolyte due to membrane barrier.

Enthalpy change $\triangle H$ for the diffusion process is given by the equation:

$$\triangle H = E_a + RT \qquad \ldots\ldots \text{(i)}$$

Free energy change, $\triangle F$ is calculated with the help of equation for the theory of absolute reaction rate for the process of diffusion as under :

$$P = \frac{\lambda_2 kT}{dh} . e^{-\triangle F/RT} \qquad \ldots\ldots \text{(ii)}$$

where P = permeability in cms. per sec., k = Boltzmann constant, d = thickness of the membrane, $\lambda = 3 \times 10^{-8}$ cm. (by Lai and Mortland) [10] and h = average distance between two equilibrium position during the diffusion process.

Entropy change, $\triangle S$ for the diffusion process is calculated from the equation:

$$\triangle F = \triangle H - T\triangle S \qquad \ldots\ldots \text{(iii)}$$

The negative values of $\triangle S$ as compared with those observed in case of parchment-supported membrane indicate either the formation of covalent bond

between the permeating species and the membrane material or that the permeation through membrane is not kinetically controlled.

It is evident from the results that the values of $\triangle F$ and $-\triangle S$ increase with the size of the ions. The sequence in case of anions is $SO_4^{--} > CNS^- > I^- > Br^- > Cl^-$ and that of cations is $K^+ > Na^+$ (alkali metal ions) and $Mg^{++} > Ca^{++} > Ba^{++}$(alkaline earth metal hydrated ions). However, regular change in $\triangle H$ is not observed. This may be due to the fact that size of the ions is not the only factor controlling the diffusion process through the membrane. Besides size of the ion, the charge on the membrane, its porosity, charge on the diffusing ion, adsorption and material also control the diffusion process.

ACKNOWLEDGEMENT Thanks are due to Shri T. R. Chadha, Principal M L.N. College, Yamuna Nagar for encouragement.

Table-I Thermodynamic Parameters (Calculated from the transiton state theory of rate process) for electrolyte diffusion through Aluminium Ferrocyanide membrane at 25°C.

Electrolyte	E_a(KCl)	$\triangle H$(KCal)	$\triangle F$(KCal)	$\triangle S$(E.U.)
(a) Electrolytes with same cations				
KCl	7.278	6.676	7.235	-1.875
KBr	8.712	8.110	8.700	-1.980
KI	8.470	7.878	8.784	-3.040
KCNS	8.178	7.586	8.843	-4.218
K_2SO_4	8.207	6.615	8.904	-7.681
(b) Electrolytes with same anions				
NaCl	7.355	6.763	7.168	-1.359
KCl	7.278	1.676	7.235	-1.875
$MgCl_2$	9.089	8.487	8.826	-1.138
$CaCl_2$	8.710	8.118	8.636	-1.738
$BaCl_2$	6.525	5.923	8.406	-8.322

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