

Studies with Model Membrane: The Effect of Temperature on Membrane Potential

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Abstract

Membrane potentials for silver bromide parchment supported membrane at different temperatures (30 – 70°C) have been measured. Experimental results were analyzed on the basis of the Kobatake equation, and some characteristic parameters (α , β , and mobility ratios) have been evaluated. The mobility ratios of ions in the membrane phase (u_+/u_-) are found to be increased with temperature. This order may apparently lead to the conclusion that the ion size is the controlling factor and the membrane is cation exchanger. The activation energy was also obtained. The activation thermodynamics parameters, enthalpy of activation ΔH^\ddagger , entropy of activation ΔS^\ddagger and free energy of activation ΔG^\ddagger have been estimated

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1. Introduction

Transport processes occurring across artificial membranes separating different salts solutions are of great interest to chemists, chemical engineers, and biologists. Chemists and chemical engineers would like to understand the mechanism of transport so that with the knowledge so gained they would be able to fabricate membranes of any desired property or properties. Biologists, however, would like to use them as models for the physiological membranes in order to understand the behavior of complex cell membranes [1]. Several membranes have been prepared using inorganic–inorganic salt. However these inorganic membranes have sufficiently low chemical stability in acidic and alkaline medium due to dissolution of inorganic phosphate into inorganic salt [2]. Different studies on permeability, permselectivity, and fixed charge density of various inorganic precipitate membranes have provided reasonably clear picture of the functioning of these membranes in contact with simple electrolyte solutions [3-16]. In previous works, we have studied different parchment-supported membranes in order to evaluate the fixed charge density and to study the permeation of different electrolytes [17-23]. In this work, membrane potentials through silver bromide parchment supported membrane for a wide interval of concentrations and different temperatures have been studied. The results have been analyzed by means of the Kobatake equation for the membrane potential [24]. The activation energy and the mobility ratio of ions in the membrane have also been obtained.

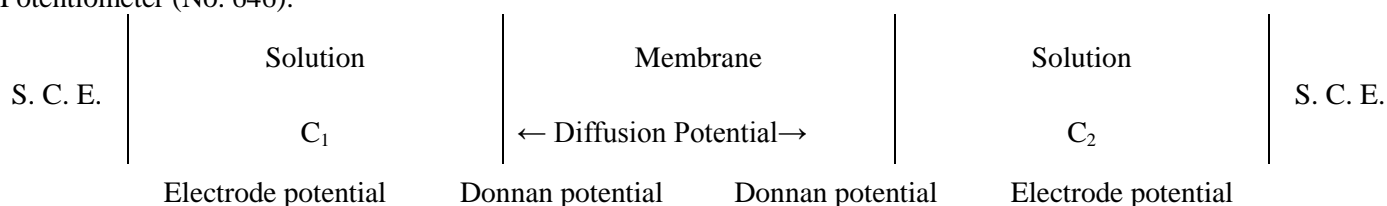
2. Materials and Methods

2.1 Preparation of Membrane

Parchment supported silver bromide membrane was prepared by the method of interaction described by Siddiqi et al. [3-6]. 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 silver nitrate solution. This was suspended for 72 hours in a 0.2 M sodium bromide solution at room temperature. The two solutions were interchanged and kept for another 72 hours. In this way fine deposition of silver bromide 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. The membrane prior to the measurements had been aged by about 24 hrs immersion in 1 M in the testing electrolyte. All the reagents used were of AR grade (BDH) and their solutions were prepared in doubly distilled water.

2.2 Membrane Potential Measurements

The potential developed by setting up a concentration cell of the type described by Siddiqi et al. [7] as in Scheme 1. The membrane potential was obtained by taking the same electrolyte at different concentrations on the two sides of the membrane, such that the concentration ratio $\sigma = 10$. The potentials were monitored by means of Knick Digital Potentiometer (No. 646).



Scheme 1. Concentration cell

Nomenclature

E_m : Membrane Potential in millivolts

u_+ and u_- : Mobilities of cation and anion, respectively, in the membrane

C_1 and C_2 : Concentrations of the electrolyte solutions on either side of the membrane

X : Charge density expressed in equivalents per liter

R : Molar gas constant

T : absolute temperature of the system

F : Faraday constant

K : Constant depend on the viscosity of the solution and structural details of the membrane

α and β : Parameters independent of salt concentration

ΔE_{mr} : Reduced membrane potential

$$\sigma = \frac{C_2}{C_1}$$

t_{-app} : Apparent transference number for co-ion in a negatively charged membrane

All measurements were carried out using a water thermostat at different temperatures (30-70°C). The solutions were vigorously stirred by a pair of magnetic stirrer in order to be maintained uniform in both the half cells. The univalent electrolytes examined were potassium chloride, potassium nitrate, ammonium nitrate, and ammonium chloride. The salt solutions were prepared from AR reagents (BDH) without further purification and using doubly distilled water

3. Results and Discussion

Membrane potentials (ΔE_m) through silver bromide membrane for a wide interval of concentration and different temperatures have been studied. The results have been analyzed by means of the Kobatake equation for membrane potential. This equation shows a relationship between the membrane potential and three parameters: X , α , and β which can be evaluated from experimental values. The parameter β is related to the fixed charge density in the membrane and a factor which depends on the viscosity of the solution and the structural details of the membrane while the parameter α is related to mobilities of cations and anions. For this reason, the Kobatake equation could be used to elucidate if the variations with temperature are due to the electrolyte solution or to change in the membrane structure. The experimentally determined membrane potential values across silver bromide membrane in contact with different concentrations of various 1:1 electrolytes at different temperatures are shown in Figures 1a, 1b, 1c, and 1d.

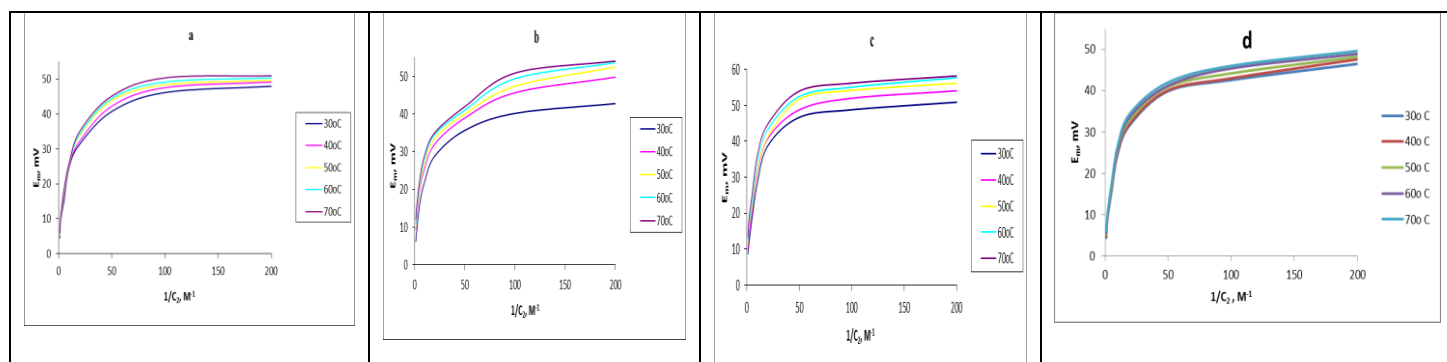


Figure 1. Membrane Potential vs. $\log(1/C_2)$ in contact with different concentrations of: (a) KCl, (b) KNO₃, NH₄NO₃, and (c) NH₄Cl

The values of apparent transference number of co-ion calculated from the membrane potential measurements and using the Nernst equation (1) are given in Tables 1a, 1b, 1c, 1d:

$$\Delta E_{nr} = (1 - 2 t_{app}) \ln \sigma \quad (1)$$

Table 1. Apparent transference number of co-ions for various electrolytes at different concentrations

(a) KCl

$(C_2/C_1) M$	t_{app}				
	30°C	40°C	50°C	60°C	70°C
1.0/0.1	0.463	0.46	0.459	0.458	0.456
0.5/0.05	0.421	0.421	0.422	0.418	0.418
0.2/0.02	0.374	0.368	0.366	0.364	0.363
0.1/0.01	0.292	0.296	0.299	0.303	0.307
0.05/0.005	0.238	0.239	0.235	0.24	0.241
0.02/0.002	0.161	0.16	0.158	0.163	0.168
0.01/0.001	0.116	0.117	0.123	0.128	0.13
0.005/0.0005	0.101	0.104	0.112	0.119	0.125

(b) KNO₃

$(C_2/C_1) M$	t_{app}				
	30°C	40°C	50°C	60°C	70°C
1.0/0.1	0.448	0.424	0.422	0.417	0.411
0.5/0.05	0.424	0.398	0.393	0.388	0.384
0.2/0.02	0.365	0.341	0.339	0.334	0.333
0.1/0.01	0.315	0.293	0.29	0.286	0.285
0.05/0.005	0.26	0.242	0.238	0.238	0.242
0.02/0.002	0.203	0.186	0.188	0.189	0.192
0.01/0.001	0.166	0.132	0.13	0.126	0.126
0.005/0.0005	0.144	0.099	0.091	0.094	0.103

(c) NH₄NO₃

$(C_2/C_1) M$	t_{app}				
	30°C	40°C	50°C	60°C	70°C
1.0/0.1	0.428	0.42	0.411	0.405	0.401
0.5/0.05	0.405	0.391	0.376	0.373	0.366
0.2/0.02	0.345	0.336	0.332	0.326	0.315
0.1/0.01	0.265	0.251	0.253	0.244	0.235
0.05/0.005	0.177	0.172	0.179	0.172	0.171
0.02/0.002	0.112	0.107	0.097	0.103	0.103
0.01/0.001	0.094	0.081	0.077	0.083	0.087
0.005/0.0005	0.077	0.065	0.062	0.063	0.073

(d) NH₄Cl

$(C_2/C_1) M$	t_{app}				
	30°C	40°C	50°C	60°C	70°C
1.0/0.1	0.463	0.461	0.459	0.458	0.455
0.5/0.05	0.425	0.424	0.424	0.423	0.422
0.2/0.02	0.374	0.373	0.374	0.373	0.373
0.1/0.01	0.295	0.299	0.3	0.303	0.303
0.05/0.005	0.236	0.241	0.243	0.244	0.246
0.02/0.002	0.168	0.177	0.181	0.188	0.192
0.01/0.001	0.146	0.154	0.155	0.157	0.162
0.005/0.0005	0.113	0.117	0.124	0.13	0.136

In Figures 2a, 2b, 2c, and 2d, $|\Delta E_{mr}|$ versus C_2 for low external concentrations at different temperatures has been drawn. The value of intercept is equal to $(1/\beta) \ln \sigma$ (Equation 2), from which β may be evaluated at each given temperature:

$$|\Delta E_{mr}| = \left(\frac{1}{\beta}\right) \ln \sigma - \left(\frac{\sigma-1}{\alpha\beta\sigma}\right) \left(1 + \frac{1}{\beta} - 2\alpha\right) \left(\frac{C_2}{X}\right) \quad (2)$$

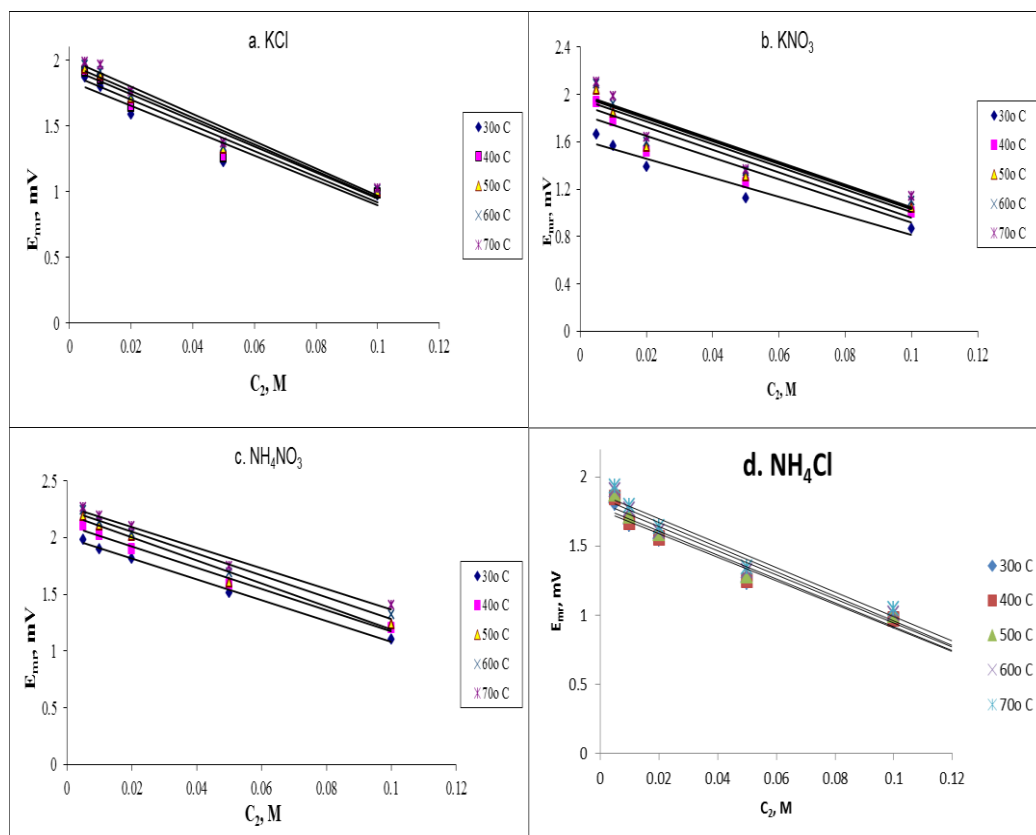


Figure 2. E_{mr} vs C_2 in contact with different electrolytes (at low concentrations)

Figures 3a, 3b, 3c, and 3d show $1/t_{app}$ as a function of $1/C_2$ at high values of the salt concentration. From the intercept of these straight lines (Equation 3), the value of α at each temperature was determined.

$$\frac{1}{t_{app}} = \frac{1}{1-\alpha} \left[\frac{(1+\beta-2\alpha\beta)(\sigma-1)\alpha}{2(1-\alpha)^2 \ln \sigma} \right] \left(\frac{X}{C_2}\right) \quad (3)$$

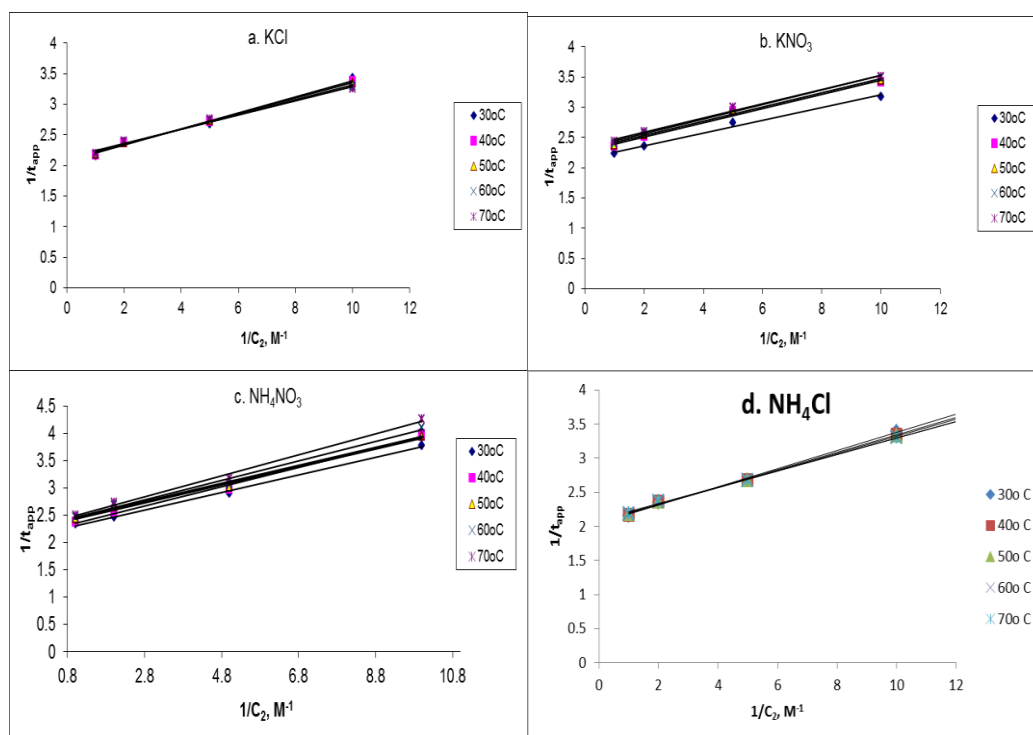


Figure 3. $1/t_{app}$ vs $1/C_2$ in contact with different electrolytes (at high concentrations)

By means of equation (4) the values of mobility ratio of ions in the membrane phase u_+/u_- , were calculated.

$$\alpha = \frac{u_+}{u_+ + u_-} \quad (4)$$

Once α and β values are known, the fixed charge in the membrane at low concentrations X_d and high concentrations X_c can be obtained from the slopes of the straight lines represented in Figures 2a, 2b, 2c, 2d, 3a, 3b, 3c, and 3d. The values of α , β , (u_+/u_-) , X_c , and X_d are shown in Tables 2, 3, and 4

Table 2. Values of α , β , X_d and X_c for KCl electrolyte at different temperatures

(°C)	α	β	(u_+/u_-)	X_d (eq. l ⁻¹)	X_c (eq. l ⁻¹)
30	0.511	1.218	1.047	0.082	0.033
40	0.518	1.222	1.073	0.080	0.031
50	0.520	1.245	1.084	0.084	0.030
60	0.527	1.264	1.113	0.079	0.028
70	0.531	1.281	1.132	0.078	0.026

Table 3. Values of α , β , X_d and X_c for KNO₃ electrolyte at different temperatures

(°C)	α	β	(u_+/u_-)	X_d (eq. l ⁻¹)	X_c (eq. l ⁻¹)
30	0.534	1.392	1.145	0.069	0.024
40	0.562	1.255	1.281	0.063	0.024
50	0.564	1.243	1.296	0.063	0.024
60	0.570	1.243	1.325	0.061	0.024
70	0.576	1.257	1.357	0.058	0.023

Table 4. Values of α , β , X_d and X_c for NH_4NO_3 electrolyte at different temperatures

($^{\circ}\text{C}$)	A	β	(u_+/u_-)	$X_d (\text{eq. l}^{-1})$	$X_c (\text{eq. l}^{-1})$
30	0.534	1.159	1.147	0.115	0.036
40	0.542	1.128	1.183	0.110	0.039
50	0.559	1.108	1.270	0.096	0.034
60	0.561	1.125	1.277	0.101	0.036
70	0.565	1.143	1.299	0.105	0.039

Table 5. Values of α , β , X_d and X_c for NH_4Cl electrolyte at different temperatures

($^{\circ}\text{C}$)	A	β	(u_+/u_-)	$X_d (\text{eq. l}^{-1})$	$X_c (\text{eq. l}^{-1})$
30	0.511	1.289	1.044	0.089	0.033
40	0.516	1.311	1.065	0.084	0.031
50	0.518	1.329	1.073	0.083	0.030
60	0.521	1.347	1.089	0.081	0.029
70	0.523	1.370	1.097	0.081	0.028

From Tables 2, 3, 4, and 5 we note that the values of the mobility ratio of the ions in the membrane phase, (u_+/u_-) , are increased with temperature, it will be seen that for the present study the following order exists: $\text{K}^+ > \text{NH}_4^+$. In case of chloride salts, mobility ratio values are low and the differences among them are also low. This order may apparently lead to the conclusion that the ion size is the controlling factor; the larger ion diffuses in the membrane phase more slowly than the smaller one and then has low mobility. The plots of $\ln(\alpha)$ of various electrolytes against $1/T$ are shown in Figure 4 from which values of energy of activation E_a are obtained and are given in Table 6. The activation thermodynamics parameters, enthalpy of activation ΔH^{\ddagger} , entropy of activation ΔS^{\ddagger} and free energy of activation ΔG^{\ddagger} have been estimated using the alternative form of Arrhenius equation given below:

$$\ln(\alpha) = \ln(K_B \cdot T/h) + (\Delta S^{\ddagger}/R) - \Delta H^{\ddagger}/T \quad (5)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger} \quad (6)$$

There h is Planck's constant and is K_B Boltzmann constant. The plots of $\ln(\alpha)$ vs. $1/T$ of various electrolytes at different temperatures for silver bromide membrane extracts gave straight lines as shown in Figure 4. The values of E_a and ΔS^{\ddagger} were calculated from the slopes and intercepts, respectively and are listed in Table 6. Where it's found that the activation energy is equal to enthalpy of activation ($E_a \sim \Delta H^{\ddagger}$). The data of present study indicate that electrolyte permeation gives rise negative values of ΔS^{\ddagger} for all the electrolytes used. The negative value of ΔS^{\ddagger} indicates electrolyte diffusion with partial immobility increases in a relative manner with increase in valence and hydrated ionic size of the permeating species.

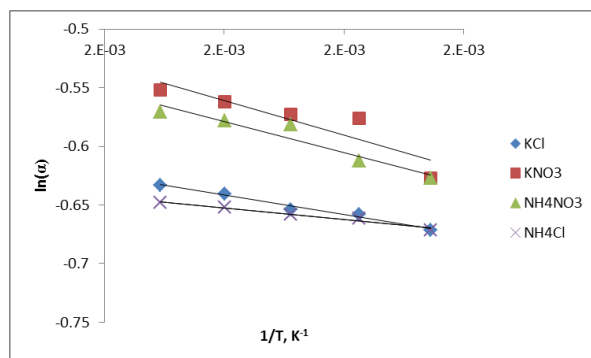
**Figure 4.** Plots of $\ln(\alpha)$ against $1/T$ of various electrolytes at different temperatures

Table 6. Experimental activation energy and other thermodynamic parameters for various electrolytes

<i>Electrolytes</i>	E_a <i>kJ mol⁻¹</i>	ΔH^\ddagger <i>kJ mol⁻¹</i>	ΔS^\ddagger <i>kJ mol⁻¹</i>	ΔG^\ddagger <i>kJ mol⁻¹</i>
KCl	2.77	2.77	-0.244	75.5
KNO ₃	4.92	4.92	-0.241	76.7
NH ₄ NO ₃	2.10	2.10	-0.243	74.5
NH ₄ Cl	1.66	1.66	-0.242	73.8

4. Conclusion

The membrane potentials across parchment supported silver bromide membrane have been measured and found to increase with temperature. The mobility ratio of the ions in the membrane phase are also increased with temperature with the following order: $K^+ > NH_4^+$. This order may apparently lead to the conclusion that the ion size is the controlling factor. The thermodynamics parameters, ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger , have been estimated using the alternative form of Arrhenius equation. The negative value of ΔS^\ddagger 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.

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