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A study of transport phenomenon of electrolytic solutions across Acroshield^{TM} composite cellophane membrane

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Studies of the hydrodynamic flow of aqueous solutions of sodium bromide, barium sulphate and inositol across the Acroshield^{TM} composite cellophane membrane are described in terms of hydrodynamic permeability values. The permeability values are interpreted in terms of a pseudo-activation process. The enthalpy of activation (ΔH^*), entropy of activation (ΔS^*), Free energy of activation (ΔG^*) have been estimated from Eyring's rate equation. The negative values of ΔS^* suggest that the flow of solutions through the membranes is more ordered which may be attributed to the greater membrane-solution interaction.

Keyword: Sodium bromide, barium sulphate, inositol, activation parameters, Acroshield^{TM} composite cellophane membrane, Eyring's rate equation.

1. Introduction

The study of transport through the membrane is being studied last three decades. New membranes have been designed relating to desalination and electrochemical devices. The transport studies have been explained with the help of thermodynamics of irreversible processes. The hydrodynamic flow of a fluid through a porous medium can either be viscous flow (developed due to pressure difference) or diffusional flow (developed due to chemical potential gradient); or a combination of the two as characterized by irreversible thermodynamics [1-6]. These flows vary exponentially with temperature. The dependence of these flows on temperature is characterized in terms of the activation energy. The present study determined activation parameters for the hydrodynamic flow of aqueous solutions of sodium bromide, barium sulphate and inositol across the Acroshield^{TM} composite cellophane membrane. In this paper, a detailed study of permeability coefficients and various activation parameters as a function of concentration and temperature has been made at varying concentrations and three different temperatures.

2. Experimental

Sodium bromide, barium sulphate and inositol of AR grade was used for making different solutions with water, which was distilled thrice over alkaline $KMnO_4$ in an all-glass apparatus. The specific conductance of water so obtained was 1.3×10^{-4} Ωcm^{-1}. The apparatus and procedure were the same as described elsewhere [7-8]. Permeability coefficient measurement was carried out in a permeation cell which was kept in an air thermostat maintained at a desired temperature within ± 0.5 ^{0}C. The thermometer was kept constant with the help of a contact thermometer an electronic relay type 1050 supplied by Anu Vidyut, Roorkee (India). The data of the rate of flow in the capillary were analysed in terms of volume flux which was further used to estimate permeability coefficient 'L_p' by using the relation as,

$$J_v = L_p \Delta P$$

Where, Jv is the volume flux per unit area of the membrane and ΔP is the pressure difference across the membrane. The hydrodynamic volume flux J_v of the solution through the membrane is estimated from the following relations.

$$Jv = \pi r^2 x / \pi R^2 t \ \ldots\ldots\ldots\ldots\ldots(1)$$

Where 'x' the distance moved in the capillary of the apparatus in time t, 'r' is the radius of the capillary and R is the radius of the membrane.

The various activation parameters, namely enthalpy of activation (ΔH*), entropy of activation (ΔS*) and free energy of activation (ΔG*) have been evaluated. The energy of activation, E_n for the flow is obtained by the slopes of the plots of log L_p v/s 1/T which is always a straight line. The activation energy may be equated to the enthalpy of activation ΔH* by applying the theory of absolute reaction rates. From this value, the entropy of activation, ΔS* may be estimated from the Eyring's rate equation for flow i.e,

$$\Delta S^* = \frac{\Delta H^*}{T} + R\log\left(\frac{Nh}{\eta\bar{V}}\right) \ \ldots\ldots\ldots\ldots(2)$$

Where 'η' is the viscosity of the permeating liquid, $\bar{V}$ is the molar volume of the permeating liquid, 'N' is the Avogadro's number, 'h' is the Planck's constant and 'R' is the gas constant. This equation is a result of eyring's rate equation. The activation free energy, ΔG* may be estimated from the equation,

$$\Delta G^* = \Delta H^* - T\Delta S^* \ \ldots\ldots\ldots\ldots(3)$$

3. Results and discussion

The data show that the permeability coefficient decreases with increase in concentration in all the cases. An analysis of the values of the values of permeability coefficient shows that L_p decreases with increase in concentration. This is expected as permeability is inversely proportional to viscosity. The values of the permeability coefficient increases with increase in concentration and temperature in case of all the solution systems under consideration, indicating that water membrane interaction increases with increase in solute concentration and hence in the viscosity of the medium. The values of ΔH* increases with increase in concentration in all cases. The values of ΔS* has negative values which suggests that the flow through membrane is more ordered due to membrane solution interaction [8]. The values of ΔH* and ΔS* estimated are used for calculating the free energy of activation ΔG* using thermodynamic expressions and the values of ΔG* obtained increases as the concentration is increased. The negative values of ΔS* suggest that the flow of solutions through the membranes is more ordered which may be attributed to the greater membrane-solution interaction [9]. The necessary data of permeability and activation parameters at five different concentrations and at varying temperatures 303K, 308K and 311K has been summarised in Tables 1-6 and figures 1-9.

Table 1: Permeability Coefficient for aqueous solutions of Sodium Bromide at different concentrations and temperatures across Acroshield™ composite cellophane membrane.

L_p x 10^{12} ($m^3N^{-1}S^{-1}$)

C_1 = 5%

Pressure difference	**Temperature in Kelvin (K)**		
ΔP x 10^{-2}(Nm^{-2})	**303**	**308**	**311**
4.925	0.798	0.820	0.949
5.706	0.886	0.937	0.969
6.488	1.005	1.009	1.018
7.270	1.024	1.082	1.112
8.052	1.153	1.267	1.528

C_2 = 10%

Pressure difference	**Temperature in Kelvin (K)**		
ΔP x 10^{-2}(Nm^{-2})	**303**	**308**	**311**
4.925	0.838	0.864	0.888
5.706	0.758	0.780	0.827
6.488	0.774	0.777	0.828
7.270	0.765	0.776	0.812
8.052	0.806	0.841	0.801

C_3 = 15%

Pressure difference	**Temperature in Kelvin (K)**		
ΔP x 10^{-3}(Nm^{-2})	**303**	**308**	**311**
4.925	0.780	0.788	0.801
5.706	0.692	0.703	0.711
6.488	0.632	0.662	0.682
7.270	0.609	0.628	0.648
8.052	0.648	0.657	0.672

Table 2: Enthalpy of activation, entropy of activation and free energy of activation of activation of aqueous solutions of Sodium Bromide at different concentrations and temperatures across Acroshield™ composite cellophane membrane.

Concentration % (w/w)	$\Delta H^* \times 10^{-2}$ ($Jmole^{-1}$)	ΔS^* ($JK^{-1}mole^{-1}$)	$\Delta G^* \times 10^{-4}$ ($Jmole^{-1}$)
5%	1.11	-45.74	1.36
10%	1.33	-45.16	1.34
15%	2.33	-41.78	1.24

Table 3: Permeability Coefficient for aqueous solutions of Barium sulphate at different concentrations and temperatures across Acroshield™ composite cellophane membrane.

$L_p \times 10^{11}$ ($m^3N^{-1}S^{-1}$) C_1 = 1.0%

C_1 = 1.0%

Pressure difference $\Delta P \times 10^{-3}$(Nm^{-2})	Temperature in Kelvin (K)		
	303	308	311
2.152	4.606	5.250	5.718
2.655	4.073	5.277	5.293
3.157	3.852	4.244	4.934
3.653	3.816	4.672	4.827
4.158	3.806	4.899	4.718

C_2 = 1.5%

Pressure difference $\Delta P \times 10^{-3}$(Nm^{-2})	Temperature in Kelvin (K)		
	303	308	311
2.152	4.550	5.031	5.382
2.655	4.915	4.694	5.075
3.157	4.343	4.388	4.646
3.653	4.131	4.238	4.397
4.158	4.134	4.311	4.542

C_3 = 2.0%

Pressure difference $\Delta P \times 10^{-3}$(Nm^{-2})	Temperature in Kelvin (K)		
	303	308	311
2.152	5.018	5.298	5.556
2.655	4.452	4.740	4.995
3.157	4.367	4.573	4.627
3.653	4.193	4.414	4.328
4.158	4.014	4.215	4.069

Table 4: Enthalpy of activation, entropy of activation and free energy of activation of activation of aqueous solutions of Barium sulphate at different concentrations and temperatures across Acroshield™ composite cellophane membrane.

Concentration % (w/w)	$\Delta H^* \times 10^{-2}$ ($Jmole^{-1}$)	ΔS^* ($JK^{-1}mole^{-1}$)	$\Delta G^* \times 10^{-4}$ ($Jmole^{-1}$)
1%	2.0	-56.112	1.672
1.5%	3.6	-50.70	1.511
2.0%	4.0	-49.32	1.470

Table 5: Permeability Coefficient for aqueous solutions of Inositol at different concentrations and temperatures across Acroshield™ composite cellophane membrane.

$L_p \times 10^{11}$ ($m^3N^{-1}S^{-1}$) C_1 = 2.0%

C_1 = 2.0%

Pressure difference $\Delta P \times 10^{-3}$(Nm^{-2})	Temperature in Kelvin (K)		
	303	308	311
3.260	**1.624**	**1.745**	**1.841**
3.777	**1.490**	**1.537**	**1.691**
4.295	**1.418**	**1.492**	**1.612**
4.812	**1.439**	**1.460**	**1.781**
5.330	**1.392**	**1.415**	**1.987**

C_2 = 5.0%

Pressure difference $\Delta P \times 10^{-3}$(Nm^{-2})	Temperature in Kelvin (K)		
	303	308	311
3.260	1.516	1.637	1.620
3.777	1.334	1.484	1.549
4.295	1.266	1.412	1.494
4.812	1.244	1.414	1.505
5.330	1.161	1.404	1.465

C_3 = 10%

Pressure difference $\Delta P \times 10^{-3}$(Nm^{-2})	Temperature in Kelvin (K)		
	303	308	311
3.260	1.236	1.310	1.360
3.777	1.145	1.185	1.236
4.295	1.062	1.087	1.294
4.812	1.024	1.180	1.271
5.330	1.027	1.109	1.233

Table 6: Enthalpy of activation, entropy of activation and free energy of activation of activation of aqueous solutions of Inositol at different concentrations and temperatures across Acroshield™ composite cellophane membrane.

Concentration % (w/w)	$\Delta H^* \times 10^{-2}$ ($Jmole^{-1}$)	ΔS^* ($JK^{-1}mole^{-1}$)	$\Delta G^* \times 10^{-4}$ ($Jmole^{-1}$)
2%	2.22	-47.97	1.451
5%	3.33	-47.49	1.448
10%	3.37	-47.26	1.446

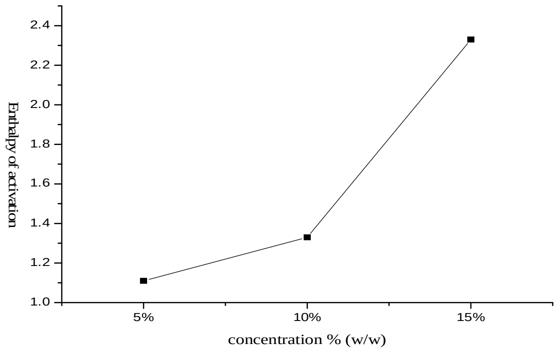

Fig 1: Plot of enthalpy of activation versus concentration for the aqueous solutions of NaBr across Acroshield^{TM} composite cellophane membrane.

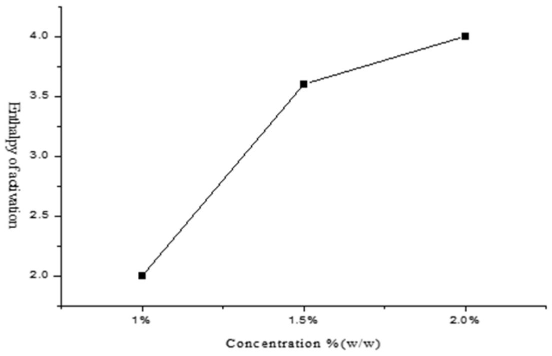

Fig 2: Plot of enthalpy of activation versus concentration for the aqueous solutions of $BaSO_4$ across Acroshield^{TM} composite cellophane membrane

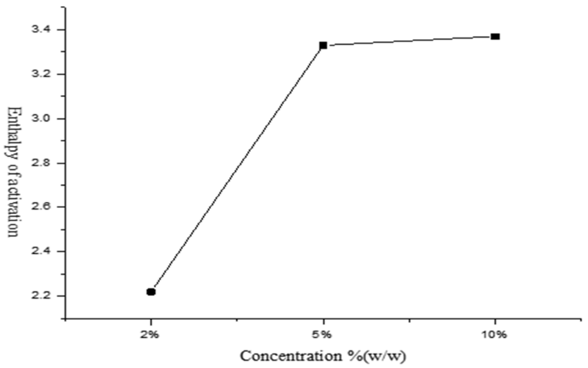

Fig 3: Plot of enthalpy of activation versus concentration for the aqueous solutions of Inositol across Acroshield^{TM} composite cellophane membrane.

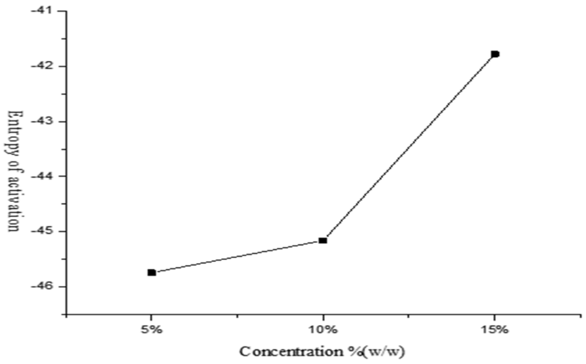

Fig 4: Plot of entropy of activation versus concentration for the aqueous solutions of NaBr across Acroshield^{TM} composite cellophane membrane

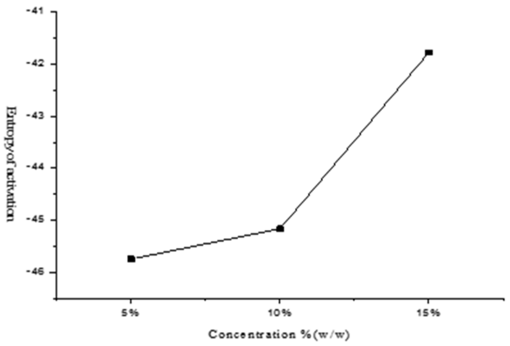

Fig 5: Plot of entropy of activation versus concentration for the aqueous solutions of $BaSO_4$ across Acroshield^{TM} composite cellophane membrane.

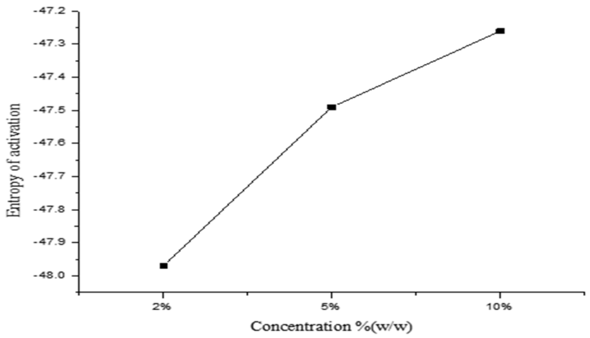

Fig 6: Plot of entropy of activation versus concentration for the aqueous solutions of Inositol across Acroshield^{TM} composite cellophane membrane.

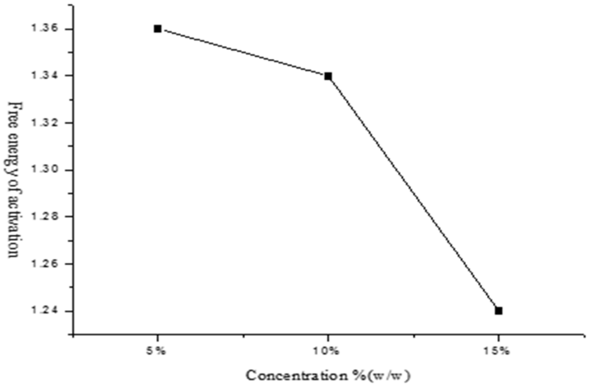

Fig 7: Plot of free energy of activation versus concentration for the aqueous solutions of NaBr across Acroshield^{TM} composite cellophane membrane.

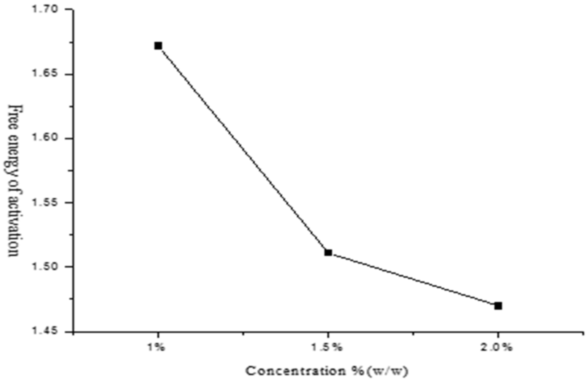

Fig 8: Plot of free energy of activation versus concentration for the aqueous solutions of $BaSO_4$ across Acroshield^{TM} composite cellophane membrane.

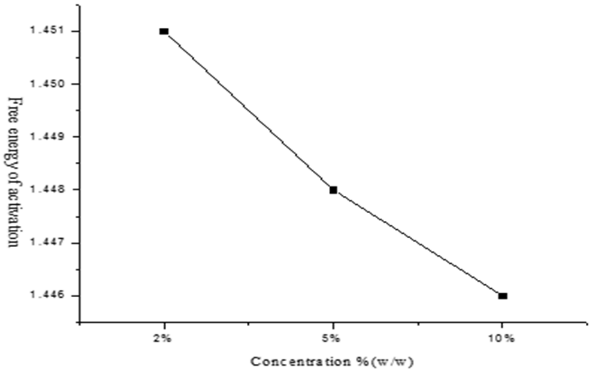

Fig 9: Plot of free energy of activation of activation versus concentration for the aqueous solutions of Inositol across Acroshield^{TM} composite cellophane membrane.

4. Conclusion

The study of transport properties of aqueous solutions of sodium bromide, barium sulphate and inositol across the Acroshield^{TM} composite cellophane membrane reflects the utility of the membranes in battery separators. The dependence of permeability and activation parameters on composition is an indication of the presence of molecular interactions between the membrane and solute particles.

5. Acknowledgement

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6. References

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