Scholars Research Library

Der Pharma Chemica, 2014, 6(4):130-134
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

A study of transport phenomenon of urea and its sulphur analogue across a naturally hydrophilic membrane

Anjali Anand* and Meena Sharma

P. G. Department of Chemistry, University of Jammu, Jammu, J & K(India)

ABSTRACT

Studies of the hydrodynamic flow of aqueous solutions of urea and its sulphur analogue i.e., thiourea through a naturally hydrophilic membrane like Nylon^{TM} Biobond 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^* suggests that the flow of solutions through the membranes is more ordered which may be attributed to the greater membrane-solution interaction.

Keywords: Urea, thiourea, permeability coefficient, activation parameters, Nylon^{TM} Biobond membrane, Eyring's rate equation.

INTRODUCTION

The study of transport through 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 Urea and Thiourea across Nylon^{TM} Biobond 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 four different temperatures.

MATERIALS AND METHODS

Urea and thiourea 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 $1.3\times10^{-4}\ \Omega cm^{-1}$. 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℃. The thermometer was kept constant with the help of a contact thermometer an electronic relay type 1050 supplied by Anu Vidyut, Roorkee. 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 J_v 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.

$$J_v = \pi r^2 x / \pi R^2 t \qquad (1)$$

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.,

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

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,

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

RESULTS AND DISCUSSION

The data shows that permeability coefficient decreases with increase in concentration in all the cases. An analysis 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 both urea and thiourea, indicating that water membrane interaction increases with increase in solute concentration and hence in the viscosity of the medium. Different membranes used in alternate energy devices have been characterized in terms of parameters of activation i.e. ΔH*, ΔS* and ΔG*. 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* suggests that the flow of solutions through the membranes is more ordered which may be attributed to the greater membrane-solution interaction [9]. Also the behaviour shown by ΔH* and ΔS* values suggest that solute and solvent molecules are strongly associated. The necessary data of permeability and activation parameters at five different concentrations(2.5%, 3.5%, 4.5%, 5.5% and 6.5%) and at varying temperatures 303K, 308K, 311K and 313K has been summarised in Tables 1-4 and figures 1-5.

Table 1 Permeability Coefficient for aqueous solutions of Urea at different concentrations and temperatures across Nylon^{TM} Biobond membrane
L_p x 10^{11} ($m^3N^{-1}S^{-1}$)

C_1 = 2.5%

Pressure difference	**Temperature in Kelvin (K)**			
ΔP x 10^{-3}(Nm^{-2})	**303**	**308**	**311**	**313**
0.83	10.70	11.40	11.58	12.55
1.00	9.43	9.99	11.34	12.15
1.17	9.18	9.97	11.00	11.69
1.34	8.73	9.91	10.60	11.43

C_2 = 3.5%

Pressure difference	**Temperature in Kelvin (K)**			
ΔP x 10^{-3}(Nm^{-2})	**303**	**308**	**311**	**313**
0.83	8.40	9.00	11.10	11.95
1.00	8.00	9.20	10.74	11.65
1.17	7.90	8.20	9.90	11.59
1.34	7.20	7.80	9.06	11.06

C_3 = 4.5%

Pressure difference $\Delta P \times 10^{-3}(Nm^{-2})$	**Temperature in Kelvin (K)**			
	303	**308**	**311**	**313**
0.83	8.33	8.47	10.27	10.75
1.00	7.74	8.11	9.90	9.66
1.17	7.31	8.09	8.90	9.47
1.34	6.71	7.45	8.51	9.35

C_4 = 5.5%

Pressure difference $\Delta P \times 10^{-3}(Nm^{-2})$	**Temperature in Kelvin (K)**			
	303	**308**	**311**	**313**
0.83	7.98	8.82	9.67	10.27
1.00	7.14	8.45	9.25	9.96
1.17	7.06	7.69	8.27	8.96
1.34	6.41	7.67	7.60	8.29

C_5 = 6.5%

Pressure difference $\Delta P \times 10^{-3}(Nm^{-2})$	**Temperature in Kelvin (K)**			
	303	**308**	**311**	**313**
0.83	7.62	8.11	9.31	9.65
1.00	6.94	8.05	8.46	8.76
1.17	6.46	7.49	9.93	8.11
1.34	6.00	7.23	7.46	8.07

Table 2 Permeability Coefficient for aqueous solutions of Thiourea at different concentrations and temperatures across Nylon^{TM} Biobond membrane

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

C_1 = 2.5%

Pressure difference $\Delta P \times 10^{-3}(Nm^{-2})$	**Temperature in Kelvin (K)**			
	303	**308**	**311**	**313**
0.81	10.86	11.65	13.63	14.34
0.98	10.71	11.33	12.79	13.71
1.14	9.71	11.29	12.01	13.43
1.30	9.57	10.49	11.74	12.74

C_2 = 3.5%

Pressure difference $\Delta P \times 10^{-3}(Nm^{-2})$	**Temperature in Kelvin (K)**			
	303	**308**	**311**	**313**
0.81	8.90	9.15	10.48	11.42
0.98	8.12	8.53	9.57	11.16
1.14	7.93	8.77	9.56	11.12
1.30	7.70	8.13	9.12	10.77

C_3 = 4.5%

Pressure difference $\Delta P \times 10^{-3}(Nm^{-2})$	**Temperature in Kelvin (K)**			
	303	**308**	**311**	**313**
0.81	8.12	9.01	9.10	10.67
0.98	7.76	8.51	9.98	11.08
1.14	6.91	7.68	8.72	10.37
1.30	6.63	7.62	8.53	10.26

C_4 = 5.5%

Pressure difference $\Delta P \times 10^{-3}(Nm^{-2})$	**Temperature in Kelvin (K)**			
	303	**308**	**311**	**313**
0.81	7.83	8.91	8.92	9.89
0.98	7.02	7.92	8.73	9.83
1.14	6.70	7.70	8.24	8.51
1.30	5.93	7.50	7.58	7.66

C_5 = 6.5%

Pressure difference $\Delta P \times 10^{-3}(Nm^{-2})$	**Temperature in Kelvin (K)**			
	303	**308**	**311**	**313**
0.81	6.98	7.56	7.79	8.03
0.98	6.47	6.67	7.25	7.82
1.14	6.03	5.96	7.02	7.18
1.30	5.56	5.85	6.56	6.78

Table 3 Enthalpy of activation, entropy of activation and free energy of activation of activation of aqueous solutions of Urea at varying concentrations across Nylon™ Biobond membrane

Concentration % (w/w)	$\Delta H^{*} \times 10^{-2}$(Jmole^{-1})	ΔS^{*} (JK^{-1}mole^{-1})	$\Delta G^{*} \times 10^{-4}$(Jmole^{-1})
2.5	20.75	-108.46	34.93
3.5	26.41	-106.74	34.98
4.5	28.30	-106.25	35.02
5.5	29.43	-106.50	35.07
6.5	30.00	-106.10	35.11

Table 4 Enthalpy of activation, entropy of activation and free energy of activation of activation of aqueous solutions of Thiourea at varying concentrations across Nylon™ Biobond membrane

Concentration % (w/w)	$\Delta H^{*} \times 10^{-2}$(Jmole^{-1})	ΔS^{*} (JK^{-1}mole^{-1})	$\Delta G^{*} \times 10^{-4}$(Jmole^{-1})
2.5	13.20	-110.87	34.91
3.5	28.30	-105.91	34.92
4.5	30.18	-105.40	34.95
5.5	39.62	-102.49	35.01
6.5	41.50	-102.16	35.10

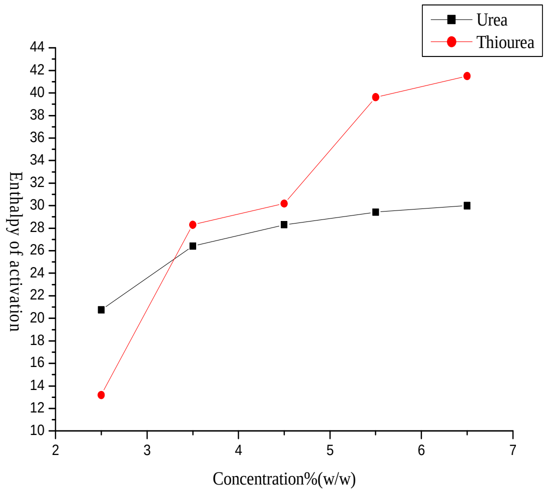

Fig 1: Plot of concentration versus Enthalpy of activation for aqueous solutions of urea and thiourea at varying concentrations across Nylon™ Biobond membrane

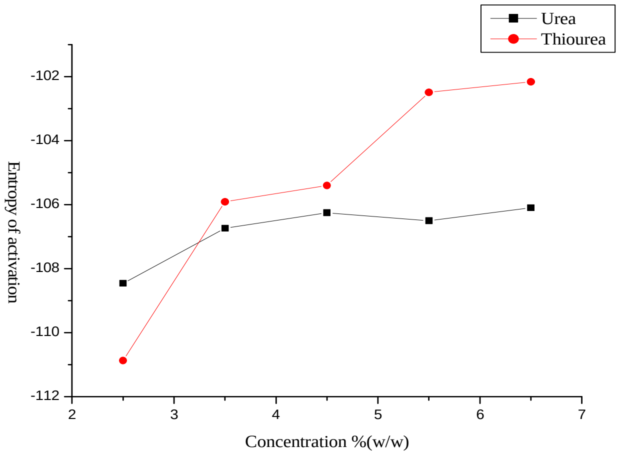

Fig 2: Plot of concentration versus Entropy of activation for aqueous solutions of urea and thiourea at varying concentrations across Nylon™ Biobond membrane

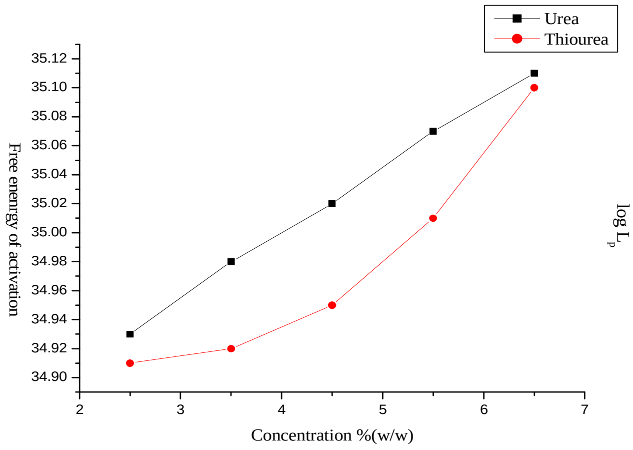

Fig 3: Plot of concentration versus free energy of activation for aqueous solutions of urea and thiourea at varying concentrations across Nylon™ Biobond membrane

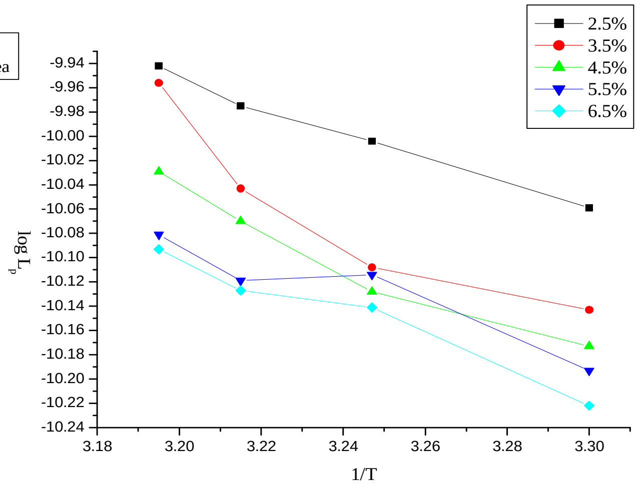

Fig 4: Plot of log L_P v/s 1/T for aqueous solutions of urea at different temperatures and concentrations across across Nylon™ Biobond membrane

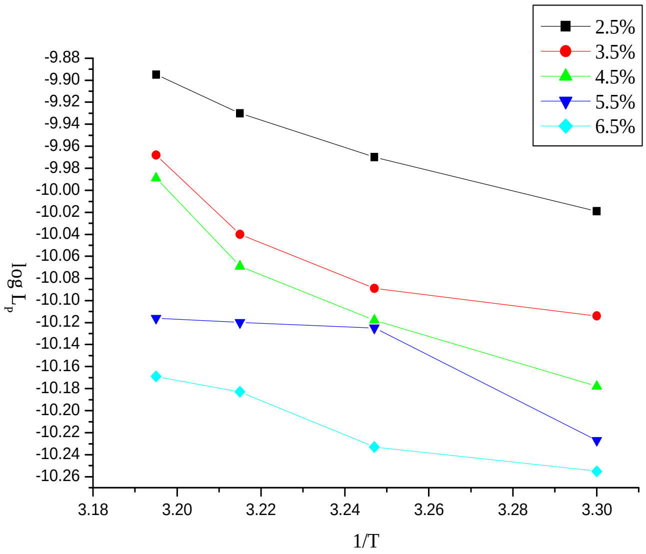

Fig 5: Plot of log L_P v/s 1/T for aqueous solutions of thiourea at different temperatures and concentrations across across Nylon^{TM} Biobond membrane

CONCLUSION

The study of transport properties of aqueous solutions of urea and thiourea across Nylon^{TM} Biobond 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.

Acknowledgement
The authors are thankful to the P.G. Department of Chemistry, University of Jammu for providing necessary lab facilities.

REFERENCES

[1] V. Buckin, B. Driscoll, C. Smyth, Ultrasonic spectroscopy for material analysis. Recent Analysis, Spectroscopy Europe, **2003**, 20.
[2] I.G. Michailov, V.A. Solovjev, Y.P. Syrnikov, Fundamentals of molecular acousties, Moscow, **1988**, 516.
[3] B.E. Conway, Ionic hydration in Chemistry, Elsevier, Amsterdam, **1981**.
[4] T.V. Chalikian, A.P. Sarvazyan, K.J. Breslauer, *Biophys. Chem.*, **1994**, 51, 89.
[5] U. Kaatze, T.O. Husheha, F. Eggers, Ultrasonic broad band spectrometry of liquids. *Journal for solution chemistry*, **2000**, 29, 299.
[6] U. Kaatze et. al, *Sci. Technol.* (EJ), **2001**, 19, 6.
[7] N. Lakshminarayaniah, Transport Phenomenon in Membrane, Academic Press, New York, **1969**, 313.
[8] R. Hasse, Thermodynamics of irreversible Processes, Reading Massachusetts, **1969**, 177.
[9] S.A. Schichman, R.L. Amey, *J. Phys. Chem.*, **1971**, 75, 98.