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STUDY ON TRANSPORT PHENOMENON OF SOME DIVALENT TRANSITION METAL SULPHATES AND MAGNESIUM SULPHATE IN BINARY AQUEOUS MIXTURES OF DIETHYLENE GLYCOL (DEG)

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Abstract

In order to explain the transport phenomenon across diaphragms understanding of non equilibrium thermodynamics is very important and in the present study non – equilibrium thermo – dynamic treatment is used to analyse the transport phenomenon of transition metal sulphates (divalent) and magnesium sulphate in mixtures of diethylene glycol (DEG)+water through an inorganic membrane of an aluminium oxide. Activation parameters (ΔH^*,ΔS^*, ΔG^*) including filtration coefficients (Lp) are also determined in 5% (w/w) DEG+water at different temperatures in order to predict the spontaneiety of the liquid flow through the membrane.

Keywords **:**Transport phenomenon, non – equilibrium thermo – dynamic treatment, filtration coefficient, activation parameters

Introduction

In order to explain the transport phenomenon across diaphragms understanding of non equilibrium thermodynamics is important. Non – equilibrium thermo – dynamic treatment (Blokhra *et al.*, 1974; Srivastava *et al.*, 1976) is generally applied to study transport phenomena under the influence of hydrodynamic pressure and electric field. Different coupled transport phenomenon are observed when potential and pressure gradient are coupled with each other where as when two different phases are brought in contact with each other different electro-kinetic effects are observed at the interfacial boundary (Delgado *et al.,* 2007; Hunter, 1981; Rastogi *et al.,* 2007; Lakshminarayaniah *et al*.,1965; Lakshminarayaniah *et al*., 1969). Some of the electro kinetic phenomena have been reported by Spiegler (Spiegler, 1958) using principles of non-equilibrium thermodynamics where as Kiran (Kiran *et al*., 2012) and others (Robbins, 1960; Mika *et al*., 2002; Thakur *et al*., 2017; Lakshminarayaniah *et al*., 1971) reported various other transport phenomenon across different types of membranes. In order to understand different transport phenomenon it becomes essential to analyse different structural details of the membrane like effective cross-sectional area, equivalent pore radius and the electrical characterstics.There are various factors like molecular size of the permeating fluid, pores in number of the membrane, density and viscosity of the permeant and state of aggregation of the liquid which affect the flow of a liquid significantly through a memberane. In the present study binary aqueous solutions of diethylene (DEG) have been taken because DEG is completely miscible in water and other organic solvents and has many applications in organic chemistry. It is used in the polymer and cosmetic industry and sometimes as a coolant with the combination of ethylene glycol. On the other hand transition metal ions are taken in the present study because these are very important in biological processes and play important role in life systems and also present in different enzymes, minerals and proteins. Magnesium sulphate has been taken as a reference divalent metal sulphate. So, it becomes important to study the transport phenomenon of these transition metal sulphates as well as magnesium sulphate in 5% (w/w) DEG + water mixtures at different temperatures.

Material and Methods

All the chemicals used in the present study were procured from S.D Fine-chem Ltd(India) and specifications are similar as mentioned by Thakur and others (Thakur *et al*., 2017) in Table.1 except DEG which is mentioned in Table1. Preparation of membrane, its calibration, other experimental details and set up for the present study is similar as used by Thakur and others (Thakur *et al*., 2017) in their study on hydrodynamic permeability.

Results and Discussion

Values of hydrodynamic permeabilties of different metal sulphates in 5% (w/w) DEG+water are determined at equidistant temperatures 298.15-318.15 K through the membrane. Hydrodynamic permeabilities of the permeating fluids vary exponentially (Glastone *et al*., 1941) with temperature and is characterized in term of activation energy (Barrer, 1941). Activation energy parameters for different ternary solutions are also determined at different temperatures. By using the experimental set up as shown in Fig.1, Volume flow 'J_v' per unit area of the membrane is measured for all the metal sulphates in 5% (w/w) DEG +water mixtures and values are recorded in Table 2.

It is found that volume flow 'J_v' varies linearly with pressure difference ΔP, for all the metal sulphates in binary aqueous mixtures of DEG at different temperatures and a sample plot of J_v vs ΔP for cobalt sulphate in 5% (w/w) DEG + water at 303.15K is shown in Fig. 2.

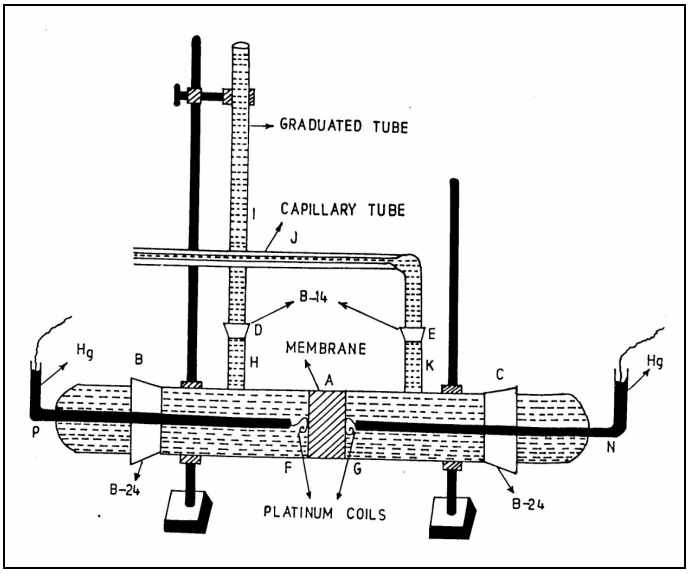

Fig. 1 : Experimental Set up

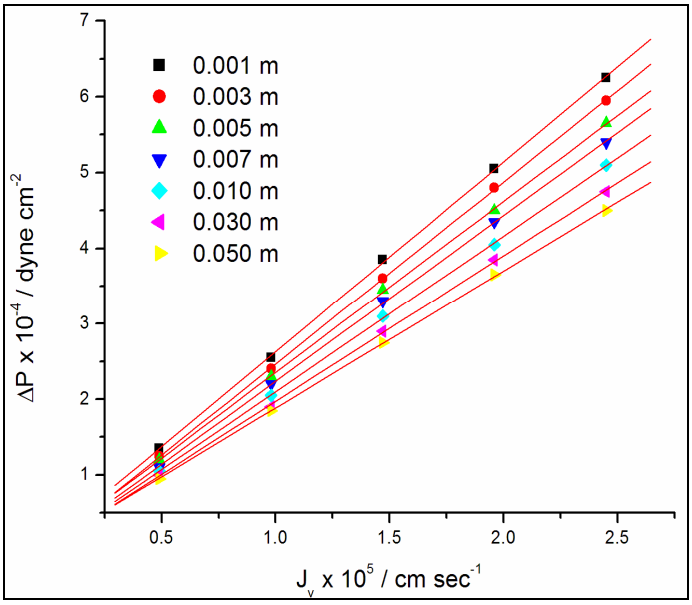

Fig. 2: Plots of J_v vs ΔP for cobalt sulphate in 5% (w/w) DEG + water mixture at 303.15K

Table 1: Specification of the Chemicals

Chemical Name	CAS No.	Molar mass (g/mol)	Mass fraction Purity
Diethylene Glycol (DEG)	111- 46- 6	106.12	≥ 0.99

Table 2: Volume Flow 'J_v' values for different metal sulphates sulphates in 5% (w/w) DEG + water at different pressures and temperatures.

ΔP x 10^{-4} dyne cm^{-2}	Jv x 10^5 / cm sec^{-1} m / mol. kg^{-1}						
	0.001	0.003	0.005	0.007	0.010	0.030	0.050
Manganese sulphate Temperature = 298.15 K							
0.49	1.35	1.25	1.20	1.15	1.08	1.00	0.95
0.98	2.60	2.40	2.25	2.15	2.00	1.95	1.80
1.47	3.90	3.60	3.40	3.20	3.00	2.80	2.60
1.96	5.20	4.80	4.50	4.25	4.00	3.75	3.40
2.45	6.40	5.95	5.65	5.30	5.00	4.60	4.30
Temperature = 303.15 K							
0.49	1.50	1.45	1.40	1.35	1.25	1.15	1.07
0.98	2.75	2.60	2.50	2.32	2.20	2.05	1.90
1.47	4.15	3.90	3.75	3.50	3.35	3.10	2.95
1.96	5.49	5.20	4.95	4.70	4.40	4.15	3.90
2.45	6.75	6.40	6.15	5.85	5.50	5.20	4.85
Temperature = 308.15 K							
0.49	1.45	1.40	1.35	1.30	1.20	1.10	1.05
0.98	2.85	2.75	2.55	2.40	2.35	2.20	2.10
1.47	4.30	4.05	3.80	3.70	3.50	3.30	3.10
1.96	5.70	5.35	5.10	4.85	4.65	4.40	4.15
2.45	7.00	6.65	6.30	6.10	5.75	5.50	5.20
Temperature = 313.15 K							
0.49	1.55	1.50	1.45	1.40	1.25	1.15	1.05
0.98	2.95	2.80	2.65	2.50	2.35	2.20	2.15
1.47	4.45	4.20	4.00	3.80	3.55	3.35	3.10
1.96	5.90	5.60	5.30	5.00	4.70	4.40	4.10
2.45	7.20	6.70	6.50	6.15	5.75	5.60	5.20
Temperature = 318.15 K							
0.49	1.60	1.55	1.45	1.35	1.30	1.20	1.15
0.98	3.00	2.85	2.65	2.50	2.40	2.25	2.10
1.47	4.60	4.35	4.10	3.90	3.70	3.50	3.20
1.96	6.00	5.80	5.45	5.20	4.90	4.60	4.60
2.45	7.55	7.20	6.80	6.50	6.15	5.75	5.35
Cobalt sulphate Temperature = 298.15 K							
0.49	1.20	1.15	1.10	1.00	0.95	0.80	0.75
0.98	2.30	2.20	2.05	1.90	1.80	1.65	1.60
1.47	3.45	3.30	3.10	2.90	2.80	2.60	2.40
1.96	4.55	4.35	4.15	3.80	3.70	3.40	3.20
2.45	5.70	5.40	5.15	4.80	4.55	4.30	3.95
Temperature = 303.15 K							
0.49	1.35	1.25	1.20	1.10	1.05	1.00	0.95
0.98	2.55	2.40	2.30	2.20	2.05	1.90	1.85
1.47	3.85	3.60	3.45	3.30	3.10	2.90	2.75
1.96	5.05	4.80	4.50	4.35	4.05	3.85	3.65
2.45	6.25	5.95	5.65	5.40	5.10	4.75	4.50
Temperature = 308.15 K							
0.49	1.40	1.35	1.25	1.15	1.10	1.05	1.00
0.98	2.60	2.50	2.35	2.25	2.20	2.05	2.00
1.47	3.95	3.75	3.60	3.45	3.30	3.15	3.00
1.96	5.20	5.00	4.75	4.60	4.35	4.20	4.00
2.45	6.45	6.20	6.00	5.25	5.45	5.20	4.75
Temperature = 313.15 K							
0.49	1.45	1.40	1.35	1.25	1.20	1.10	1.05
0.98	2.75	2.60	2.50	2.40	2.25	2.20	2.05
1.47	4.20	4.00	3.75	3.70	36.50	3.30	3.10
1.96	5.50	5.25	5.00	4.80	4.60	4.35	4.20
2.45	6.75	6.50	6.20	6.00	5.80	5.50	5.10
Temperature = 318.15 K							
0.49	1.70	1.55	1.40	1.30	1.20	1.15	1.08
0.98	2.10	2.90	2.75	2.55	2.40	2.25	2.10
1.47	4.60	4.30	4.15	3.95	3.65	3.50	3.55
1.96	6.00	5.75	5.50	5.20	4.95	4.60	4.30
2.45	7.35	7.05	6.75	6.40	6.10	5.70	5.40
Nickel sulphate Temperature = 298.15 K							
0.49	1.10	1.05	0.98	0.93	0.88	0.83	0.75
0.98	2.10	2.00	1.90	1.75	1.70	1.60	1.50
1.47	3.20	3.00	2.80	2.65	2.55	2.35	2.25
1.96	4.20	4.00	3.75	3.60	3.40	3.25	3.00
2.45	5.25	4.95	4.75	4.50	4.30	4.05	3.75
Temperature = 303.15 K							
0.49	1.15	1.10	1.00	0.90	0.80	0.75	0.72
0.98	2.20	2.10	2.00	1.85	1.65	1.60	1.50
1.47	3.35	3.15	3.00	2.75	2.60	2.40	2.25
1.96	4.40	4.15	3.95	3.70	3.40	3.20	3.00

2.45	5.50	5.20	4.90	4.60	4.25	4.00	3.75
Temperature = 308.15 K							
0.49	1.25	1.20	1.15	1.10	1.05	0.90	0.80
0.98	2.35	2.25	2.10	2.00	1.90	1.80	1.60
1.47	3.55	3.35	3.20	3.05	2.90	2.75	2.55
1.96	4.75	4.50	4.25	4.05	3.90	3.70	3.45
2.45	5.75	5.50	5.25	5.05	4.85	4.65	4.35
Temperature = 313.15 K							
0.49	1.30	1.25	1.20	1.15	1.10	0.93	0.85
0.98	2.50	2.40	2.20	2.10	1.95	1.85	1.75
1.47	3.75	3.50	3.30	3.15	3.00	2.80	2.65
1.96	4.95	4.60	4.35	4.15	3.90	3.70	3.50
2.45	6.10	5.90	5.50	5.25	4.90	4.60	4.40
Temperature = 318.15 K							
0.49	1.35	1.30	1.25	1.20	1.14	0.98	0.90
0.98	2.55	2.45	2.25	2.20	2.10	2.00	1.85
1.47	3.85	3.70	3.45	3.25	3.15	2.90	2.75
1.96	5.10	4.85	4.50	4.25	4.15	3.90	3.70
2.45	6.35	6.00	5.70	5.40	5.15	4.85	4.55
Copper sulphate **Temperature = 298.15 K**							
0.49	1.20	1.15	1.10	1.00	0.95	0.90	0.85
0.98	2.35	2.30	2.10	2.00	1.90	1.80	1.60
1.47	3.50	3.35	3.20	3.05	2.90	2.70	2.50
1.96	4.60	4.45	4.25	4.05	3.80	3.60	3.35
2.45	5.75	5.50	5.25	5.00	4.75	4.50	4.10
Temperature = 303.15 K							
0.49	1.25	1.20	1.10	1.00	0.95	0.85	0.83
0.98	2.35	2.20	2.10	2.00	1.90	1.80	1.70
1.47	3.55	3.35	3.15	3.00	2.85	2.65	2.55
1.96	4.75	4.51	4.27	3.98	3.80	3.60	3.40
2.45	6.05	5.70	5.35	5.10	4.80	4.55	4.35
Temperature = 308.15 K							
0.49	1.35	1.25	1.20	1.10	1.05	1.00	0.90
0.98	2.50	2.40	2.35	2.20	2.10	1.95	1.85
1.47	3.95	3.25	3.50	3.35	3.20	3.10	2.80
1.96	5.20	4.90	4.60	4.45	4.25	4.00	3.75
2.45	6.35	6.00	5.75	5.55	5.25	5.00	4.55
Temperature = 313.15 K							
0.49	1.40	1.35	1.25	1.20	1.15	1.10	0.95
0.98	2.70	2.55	2.40	2.35	2.20	2.10	1.95
1.47	4.00	3.85	3.70	3.55	3.30	3.15	2.95
1.96	5.30	5.00	4.85	4.65	4.40	4.15	3.90
2.45	6.60	6.35	6.10	65.80	5.50	5.25	4.70
Temperature = 318.15 K							
0.49	1.45	1.40	1.35	1.20	1.15	1.10	1.05
0.98	2.75	2.60	2.50	2.40	2.25	2.15	2.00
1.47	4.15	3.90	3.75	3.65	3.50	3.30	3.10
1.96	5.50	5.25	5.00	4.85	4.60	4.35	4.10
2.45	6.75	6.50	6.20	6.00	5.75	5.40	4.95
Zinc sulphate **Temperature = 298.15 K**							
0.49	1.10	1.00	0.95	0.90	0.85	0.80	0.75
0.98	2.15	2.00	1.90	1.75	1.65	1.60	1.50
1.47	3.20	3.00	2.85	2.75	2.55	2.45	2.25
1.96	4.25	4.00	3.80	3.60	3.45	3.20	3.00
2.45	5.25	5.00	4.75	4.50	4.25	4.00	3.75
Temperature = 303.15 K							
0.49	1.20	1.15	1.05	1.00	0.90	0.85	0.80
0.98	2.25	2.10	2.00	1.90	1.75	1.65	1.50
1.47	3.35	3.20	3.05	2.85	2.65	2.55	2.40
1.96	4.45	4.20	4.00	3.80	3.50	3.35	3.10
2.45	5.50	5.20	5.00	4.75	4.60	4.20	3.90
Temperature = 308.15 K							
0.49	1.25	1.20	1.15	1.10	1.00	0.90	0.85
0.98	2.35	2.25	2.10	2.00	1.80	1.70	1.60
1.47	3.50	3.30	3.20	3.00	2.80	2.60	2.50
1.96	4.60	4.40	4.20	4.00	3.75	3.50	3.25

2.45	5.75	5.50	5.25	5.00	4.70	4.30	4.10
Temperature = 313.15 K							
0.49	1.30	1.25	1.20	1.15	1.05	0.90	0.85
0.98	2.45	2.40	2.25	2.15	2.00	1.85	1.70
1.47	3.75	3.55	3.40	3.25	3.00	2.80	2.60
1.96	4.95	4.70	4.50	4.30	4.00	3.75	3.45
2.45	6.05	5.80	5.55	5.35	5.00	4.75	4.25
Temperature = 318.15 K							
0.49	1.45	1.35	1.30	1.25	1.15	1.10	1.05
0.98	2.95	2.75	2.60	2.45	2.35	2.20	2.00
1.47	4.20	4.00	3.80	3.70	3.50	3.25	3.10
1.96	5.50	5.25	5.05	4.80	4.60	4.40	4.00
2.45	6.80	6.50	6.30	6.05	5.80	5.45	5.05
Magnesium sulphate **Temperature = 298.15 K**							
0.49	1.15	1.05	0.95	0.85	0.80	0.75	0.70
0.98	2.20	2.15	2.00	1.90	1.80	1.65	1.55
1.47	3.30	3.15	3.00	2.80	2.70	2.45	2.35
1.96	4.35	4.20	3.95	3.75	3.60	3.30	3.10
2.45	5.45	5.20	4.95	4.70	4.50	4.15	3.80
Temperature = 303.15 K							
0.49	1.25	1.15	1.10	1.00	0.95	0.88	0.80
0.98	2.30	2.20	2.10	2.00	1.85	1.75	1.60
1.47	3.50	3.35	3.15	3.00	2.80	2.65	2.50
1.96	4.65	4.40	4.15	4.95	3.70	3.50	3.25
2.45	5.75	5.45	5.20	4.95	4.60	4.35	4.05
Temperature = 308.15 K							
0.49	1.30	1.20	1.10	1.00	0.95	0.90	0.85
0.98	2.45	2.35	2.20	2.15	2.05	1.90	1.75
1.47	3.75	3.60	3.35	3.20	3.00	2.85	2.65
1.96	4.90	4.70	4.40	4.25	4.00	3.70	3.50
2.45	6.00	5.80	5.50	5.25	5.00	4.70	4.30
Temperature = 313.15 K							
0.49	1.35	1.25	1.13	1.05	1.03	0.97	0.93
0.98	2.55	2.45	2.30	2.20	2.10	2.00	1.80
1.47	3.85	3.65	3.50	3.40	3.20	3.00	2.80
1.96	5.05	4.85	4.65	4.50	4.20	4.00	3.70
2.45	6.30	6.00	5.80	5.55	5.25	4.90	4.50
Temperature = 318.15 K							
0.49	1.45	1.40	1.35	1.25	1.15	1.10	1.00
0.98	2.80	2.70	2.50	2.40	2.30	2.10	1.90
1.47	4.25	4.00	3.90	3.70	3.50	3.20	2.90
1.96	5.60	5.35	5.15	4.85	4.60	4.25	3.90
2.45	7.00	6.60	6.40	6.10	5.75	5.30	4.75

Filtration Coefficient or permeability Coefficient (L_P)

Expression for volume flow (J_v) is given by the following equation (Jarzynska *et al.,* 2009).

$$J_V = L_p \Delta P - \sigma L_p \Delta\pi \qquad ...(1)$$

where the symbols have their usual meaning.

Filtration coefficient, L_p, at $\Delta\pi = 0$ is given by the expression:

$$L_p = \left[\frac{J_V}{\Delta P}\right]_{\Delta\pi=0} \qquad ...(2)$$

From the above equations it is clear that volume transported per unit area of the membrane per unit time, must vary linearly with the pressure difference ΔP, the membrane and same has been found true in the present study for all the ternary solutions at different temperatures. Values of permeability coefficient, L_P have been determined from the slopes of linear plots of J_v vs ΔP for the different ternary solutions and are recorded in Table. 3.

The variation of L_P with concentration for all the ternary solutions has been found linear at different temperatures. The compatibility of relation (3) given below

$$(Jv)_{\Delta\Pi=0} = L_p \Delta F \quad ...(3)$$

And according to Poissuille's law

$$L_p = \Pi \sum_{i=1}^{i=n} r_i^4 / 8\eta l \quad ...(4)$$

Here r = radius of i^{th} capillary,

n = no. of pores in the membrane matrix,

η = coefficient of viscosity of permeating fluid

l = thickness of the membrane.

Dependance of viscosity of fluid on temperature is given by the following relation:

$$\eta = Ae^{En}/RT \quad ...(5)$$

where 'A' is a constant and 'E_n' the activation energy.

Now using relation (5) in (4) and implementing logarithm we get:

$$\text{Log } L_p = K + E_n/RT \quad (6)$$

Where $K = \log \pi \sum_{i=1}^{i=n} r_i^4 / 8Al = \text{constant}$

Values of log L_p for all the transition metal sulphates and magnesium sulphate in 5% diethylene glycol + water at different temperatures are determined and are given in Table.4.

Table 3: The mechanical filtration coefficient 'L_p' for different concentrations of metal sulphates in 5% (w/w) DEG+water mixtures at different temperatures.

m / mol kg^{-1}	$L_p \times 10^9$ / $cm^3 dyne^{-1} sec^{-1}$ Temperature				
	298.15K	303.15K	308.15K	313.15K	318.15K
Manganese sulphate					
0.001	2.592	2.702	2.847	2.949	3.040
0.003	2.408	2.551	2.674	2.746	2.908
0.005	2.276	2.439	2.541	2.622	2.755
0.007	2.122	2.316	2.459	2.490	2.653
0.010	2.008	2.184	2.327	2.357	2.490
0.030	1.837	2.082	2.245	2.225	2.337
0.050	1.694	1.951	2.112	2.071	2.163
Cobalt sulphate					
0.001	2.296	2.510	2.592	2.725	2.898
0.003	2.174	2.488	2.490	2.622	2.827
0.005	2.082	2.265	2.429	2.490	2.748
0.007	1.939	2.194	2.357	2.429	2.622
0.010	1.857	2.061	2.214	2.357	2.520
0.030	1.786	1.929	2.133	2.234	2.357
0.050	1.633	1.816	1.939	2.092	2.212
Nickel sulphate					
0.001	2.122	2.225	2.225	2.459	2.561
0.003	2.000	2.090	2.214	2.347	2.408
0.005	1.916	1.990	2.112	2.194	2.276
0.007	1.835	1.888	2.030	2.092	2.271
0.010	1.743	1.763	1.959	1.949	2.055
0.030	1.651	1.653	1.918	1.876	1.967
0.050	1.531	1.543	1.827	1.806	1.867
Copper sulphate					
0.001	2.316	2.449	2.592	2.653	2.725
0.003	2.214	2.308	2.449	2.541	2.622
0.005	2.133	2.178	2.316	2.480	2.490
0.007	2.051	2.078	2.276	2.347	2.459
0.010	1.939	1.959	2.153	2.225	2.375
0.030	1.837	1.878	1.878	1.929	2.020
0.050	1.684	1.784	1.878	1.929	2.020
Zinc sulphate					
0.001	2.122	2.204	2.297	2.449	2.704
0.003	2.040	2.082	2.194	2.326	2.612
0.005	1.939	2.202	2.102	2.235	2.541
0.007	1.847	1.918	2.000	2.153	2.439
0.010	1.795	1.867	1.908	0.020	2.357
0.030	1.632	1.714	1.755	1.959	2.225
0.050	1.530	1.692	1.663	1.745	2.041
Magnesium sulphate					
0.001	2.194	2.316	2.418	2.530	2.837
0.003	2.112	2.204	2.357	2.429	2.663
0.005	2.031	2.092	2.243	2.386	2.602
0.007	1.949	2.010	2.163	2.306	2.480
0.010	1.878	1.867	2.051	2.151	2.347
0.030	1.725	1.774	1.918	2.012	2.153
0.050	1.582	1.663	1.765	1.845	1.939

Table 4: Values of Log L_p for different concentrations of metal sulphates in 5% (w/w) DEG+water at different temperatures.

m / mol kg^{-1}	Log L_p/ $cm^3 dyne^{-1} sec^{-1}$ Temperature				
	298.15K	303.15K	308.15K	313.15K	318.15K
Manganese sulphate					
0.001	-8.588	-8.568	-8.546	-8.530	-8.517
0.003	-8.618	-8.593	-8.573	-8.561	-8.536
0.005	-8.643	-8.613	-8.595	-8.581	-8.560
0.007	-8.673	-8.635	-8.609	-8.604	-8.576
0.010	-8.697	-8.661	-8.633	-8.628	-8.604
0.030	-8.736	-8.682	-8.649	-8.853	-8.631
0.050	-8.771	-8.710	-8.675	-8.684	-8.665
Cobalt sulphate					
0.001	-8.639	-8.600	-8.586	-8.565	-8.538
0.003	-8.663	-8.611	-8.604	-8.581	-8.549
0.005	-8.682	-8.645	-8.514	-8.604	-8.561
0.007	-8.712	-8.659	-8.628	-8.675	-8.581
0.010	-8.731	-8.686	-8.655	-8.628	-8.599
0.030	-8.748	-8.715	-8.671	-8.657	-8.628
0.050	-8.787	-8.741	-8.712	-8.679	-8.655
Nickel sulphate					
0.001	-8.673	-8.653	-8.653	-8.609	-8.592
0.003	-8.699	-8.679	-8.655	-8.629	-8.618
0.005	-8.718	-8.701	-8.675	-8.659	-8.643
0.007	-8.736	-8.724	-8.693	-8.679	-8.644
0.010	-8.758	-8.753	-8.708	-8.710	-8.687
0.030	-8.782	-8.782	-8.717	-8.727	-8.706
0.050	-8.815	-8.812	-8.738	-8.743	-8.729
Copper sulphate					
0.001	-8.635	-8.611	-8.586	-8.576	-8.565
0.003	-8.655	-8.637	-8.611	-8.595	-8.582
0.005	-8.681	-8.662	-8.635	-8.606	-8.604
0.007	-8.688	-8.682	-8.643	-8.629	-8.609
0.010	-8.712	-8.708	-8.667	-8.653	-8.628
0.030	-8.736	-8.726	-8.688	-8.675	-8.657
0.050	-8.774	-8.749	-8.726	-8.715	-8.695
Zinc sulphate					
0.001	-8.673	-8.656	-8.639	-8.611	-8.568
0.003	-8.690	-8.682	-8.659	-8.633	-8.583
0.005	-8.712	-8.694	-8.677	-8.651	-8.595
0.007	-8.734	-8.717	-8.699	-8.667	-8.623
0.010	-8.746	-8.729	-8.719	-8.695	-8.628
0.030	-8.787	-8.765	-8.756	-8.708	-8.653
0.050	-8.815	-8.715	-8.779	-8.758	-8.699

Magnesium sulphate					
0.001	-8.659	-8.635	-8.617	-8.597	-8.547
0.003	-8.675	-8.657	-8.628	-8.615	-8.575
0.005	-8.692	-8.679	-8.649	-8.622	-8.585
0.007	-8.710	-8.697	-8.665	-8.637	-8.606
0.010	-8.726	-8.729	-8.688	-8.667	-8.629
0.030	-8.763	-8.751	-8.717	-8.696	-8.667
0.050	-8.801	-8.779	-8.753	-8.734	-8.712

Table 5: Activation parameters for metal sulphates in 5% (w/w) DEG + water mixtures

m / mol kg^{-1}	ΔH^* x 10^3 / kJ mol^{-1}	ΔS^*x 10^3 / kJ mol^{-1}	ΔG^*/ kJ mol^{-1}
Manganese sulphate			
0.001	-0.331	-22.552	6.836
0.003	-0.368	-22.681	6.875
0.005	-0.368	-22.687	6.877
0.007	-0.421	-22.869	6.932
0.010	-0.409	-22.840	6.924
0.030	-0.437	-22.977	6.965
0.050	-0.243	-22.371	6.782
Cobalt sulphate			
0.001	-0.445	-24.775	7.510
0.003	-0.485	-24.901	7.548
0.005	-0.531	-25.059	7.596
0.007	-0.571	-25.197	7.638
0.010	-0.605	-25.318	7.675
0.030	-0.559	-23.359	7.081
0.050	-0.613	-25.409	7.702
Nickel sulphate			
0.001	-0.391	-24.343	7.379
0.003	-0.399	-24.377	7.389
0.005	-0.361	-24.258	7.353
0.007	-0.430	-24.492	7.424
0.010	-0.346	-24.224	7.343
0.030	-0.386	-24.395	7.395
0.050	-0.451	-24.647	7.471
Copper sulphate			
0.001	-0.328	-23.869	7.235
0.003	-0.353	-23.999	7.275
0.005	-0.398	-22.883	6.937
0.007	-0.397	-22.929	6.950
0.010	-0.420	-22.939	6.954
0.030	-0.393	-22.942	6.955
0.050	-0.360	-22.974	6.964
Zinc sulphate			
0.001	-0.481	-23.379	7.086
0.003	-0.496	-23.387	7.089
0.005	-0.522	-23.395	7.092
0.007	-0.522	-23.402	7.094
0.010	-0.510	-23.410	7.096
0.030	-0.621	-23.454	7.109
0.050	-0.495	-23.486	7.119
Magnesium sulphate			
0.001	-0.493	-22.805	6.913
0.003	-0.455	-22.821	6.918
0.005	-0.511	-22.837	6.922
0.007	-0.506	-22.837	6.925
0.010	-0.483	-22.852	6.927
0.030	-0.465	-22.895	6.940
0.050	-0.420	-22.927	6.950

According to relation (6) log L_p should vary linearly when plotted against 1/T, and the same has been found true for all the ternary solutions in the present study. Sample plot of log Lp vs 1/T for different concentrations of copper sulphate in 5% DEG + water is given in Fig. 3.

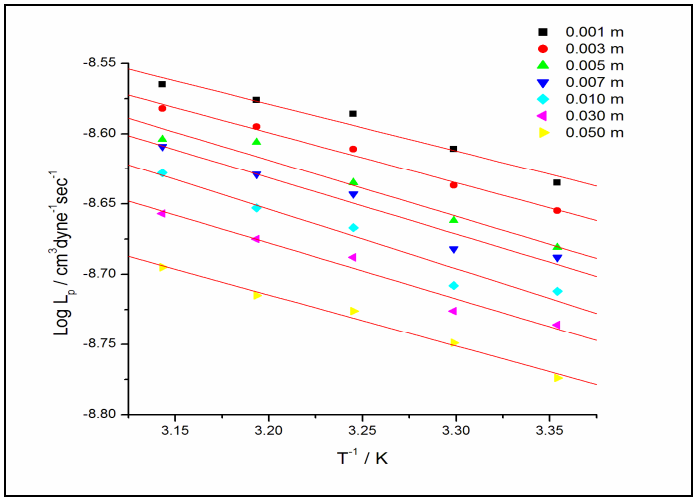

Fig. 3: Plots of Log Lp vs 1/T For copper sulphate in 5% DEG + water mixture

Activation Parameters

The values of activation energy 'E_n' are determined from the slopes of the linear plots of log $L_p$vs 1/T by using the least square method and is taken as enthalpy Δ H*, for different ternary systems and are recorded in Table. 5.

Eyring equation (Glastone *et al.*, 1941) is given by

$$\eta = \frac{Nh}{V} \exp.\left[\frac{-\Delta S^*}{R}\right] \exp.\left[\frac{-\Delta H^*}{RT}\right] \qquad ...(7)$$

where the symbols have their usual meaning.

The entropy of activation (ΔS^*) can be rearranged as follows :

$$\Delta S^* = -\frac{\Delta H^*}{T} + R\log[Nh/V\eta] \qquad ...(8)$$

In order to find different activation parameters, value of densities, viscosities and molar volumes for the different ternary solutions are also given in Table.6.

The values of entropy change ΔS* for different solutions obtained from the relation (8) are given in Table.5 and negative values show that the flow of liquid through the membrane has significant electrostatic interactions with the wall of the pores of the membrane which may be ascribed to the state of high order during the transport process of the electrolytes in binary aqueous mixtures of DEG through the membrane.

Activation parameters ΔH* and ΔS* are related to ΔG* by the expression:

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad ...(9)$$

and values of free energy change ΔG* for the ternary systems are calculated with help of relation (9) at 305.15 K, and are recorded in Table.5. Positive values of ΔG* suggest that liquid flow is not favored across the membrane and is non-spontaneous or in other words, it may be said that the flow of permitting fluid cannot take place.until an external force is applied across membrane.

Table 6 : Values of densities, viscosities and molar volumes for metal sulphates in 5% (w/w) DEG+water at 303.15K.

m / mol kg^{-1}	d / gcm^{-3}	η / cP	V / cm^3 mol^{-1}
Manganese sulphate			
0.001	1.00176	0.9009	168.71
0.003	1.00209	0.9031	168.66

0.005	1.00239	0.9050	168.61
0.007	1.00270	0.9070	168.55
0.010	1.00371	0.9099	168.48
0.030	1.00625	0.9342	167.96
0.050	1.00926	0.9358	167.46
Cobalt sulphate			
0.001	1.00178	0.9004	281.60
0.003	1.00218	0.9025	280.49
0.005	1.00255	0.9043	280.39
0.007	1.00293	0.9062	280.28
0.010	1.00349	0.9088	280.12
0.030	1.00718	0.9215	279.10
0.050	1.01075	0.9320	278.11
Nickel sulphate			
0.001	1.00177	0.9007	262.40
0.003	1.00211	0.9028	262.31
0.005	1.00242	0.9046	262.23
0.007	1.00274	0.9065	262.14
0.010	1.00323	0.9092	262.01
0.030	1.00640	0.9221	261.19
0.050	1.00749	0.9328	260.91
Copper sulphate			
0.001	1.00176	0.8807	249.25
0.003	1.00211	0.8928	249.16
0.005	1.00243	0.9047	249.08
0.007	1.00276	0.9067	249.00
0.010	1.00326	0.9095	248.88
0.030	1.00649	0.9233	248.08
0.050	1.00965	0.9346	247.30
Zinc sulphate			
0.001	1.00180	0.9007	287.04
0.003	1.00222	0.9031	286.92
0.005	1.00261	0.9052	286.81
0.007	1.00301	0.9074	286.70
0.010	1.00359	0.9101	286.53
0.030	1.00442	0.9246	285.44
0.050	1.01110	0.9362	284.40
Magnesium sulphate			
0.001	1.00173	0.8961	246.05
0.003	1.00203	0.9005	245.98
0.005	1.00230	0.9046	245.91
0.007	1.00258	0.9066	245.85
0.010	1.00299	0.9092	245.75
0.030	1.00562	0.9224	245.10
0.050	1.00818	0.9330	244.49

Conclusion

In the present study negative values of ΔS^* show that hydrodynamic flow across the inorganic membrane has significant electrostatic interactions between the walls of the pores of the membrane where as positive values of ΔG^* indicate that flow is non-spontaneous. In order words, in other words, it may be said that the flow of permitting fluid cannot take place.until an external force is applied across membrane.

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