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Activation Energy Parameters for Hydrodynamic Permeability of Divalent Transition Metal Sulphates and Magnesium Sulphate in Binary Aqueous Mixtures of Ethylene Glycol

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Due to the stable nature and applications of inorganic membranes, an aluminium oxide membrane has been used for the determination of hydrodynamic permeabilities of some divalent transition metal sulphates *e.g.*, manganese sulphate, cobalt sulphate, nickel sulphate, copper sulphate, zinc sulphate and magnesium sulphate in binary aqueous mixtures of ethylene glycol. Activation parameters of manganese sulphate, cobalt sulphate, nickel sulphate, copper sulphate, zinc sulphate and magnesium sulphate in 5 % (w/w) binary aqueous mixtures of ethylene glycol have been determined at different temperature (298.15, 303.15, 308.15, 313.15 and 318.15 K). Filtration coefficients (L_P) as a function of hydrodynamic pressure and the concentration of the solute are also determined.

Keywords: Hydrodynamic permeability, Activation parameters, Filtration coefficient.

INTRODUCTION

Coupled transport phenomenon arises due to the coupling of two forces *i.e.* potential gradient and pressure gradient which give rise to current flux and volume flux. When two different phases are brought in contact with each other, some interesting electro-kinetic effects [1,2] like streaming potential, electrophoresis sedimentation, potential (Dorn effect) and electro-osmosis are observed at the interfacial boundary. All these effects are associated with the existence of electrical double-layer at the interfacial boundary. A variety of transport phenomena arise across a membrane when it is subjected to different driving forces [3-5]. Some of these phenomena such as ion-migration, electro-osmosis, self-diffusion, hydrodynamic flow, salt filtration, streaming potential and membrane potential, *etc.* occurring across the ionic membranes have been described by Spiegler [6] by applying the principles of non-equilibrium thermodynamics.

Blokhra *et al.* [7-10] have reported the results for the transport of electrolytes and non-electrolytes across different types of diaphragm using the thermodynamics of irreversible processes. Similar results using highly charged membranes have so far not been carried out. Lakshminarayaniah [11] examined the dependence of transport numbers of water in aqueous solutions on current density using ion-exchange membrane. For proper understanding and prediction of a membrane's permeation characteristics, an insight into the structural details, *e.g.* effective cross-sectional area, equivalent pore radius and the electrical character of the membrane are required. The permeability of any membrane depends upon the molecular size of permeating fluid, number of pores of the membrane, density and viscosity of permeant, state of aggregation of liquid and the number of hydrogen bonds.

EXPERIMENTAL

Manganese sulphate, cobalt sulphate, nickel sulphate, copper sulphate, zinc sulphate and magnesium sulphate and aluminium oxide of AnalaR grade which were procured from S.D fine Chemical, Pvt. Ltd. The specifications of the above mentioned salts are given in Table-1. These chemicals were used after drying over calcium oxide for more than 24 h. The aluminium oxide was swollen in conductivity water and casted in the form of a plug. 10 g of swollen material along with small amount of an adhesive about 5 to 6 % namely araldite was placed in a pyrex glass tube having a constriction in the middle and compressed mechanically at the site of constriction with the help of a mechanical device and was left as it is for about 24 h for the complete setting of the plug. The thickness and diameter of the plug thus prepared were 1.751 cm and 1.858 cm respectively. The maximum variation in the permeability of aluminium oxide membrane prepared after one week was only of the order of 5 %. In order to know the directional nature of the membrane for the permeation of water, the flow permeability was noted in both the directions at 303.15 K and the values were found to be the same in the both the directions

TABLE-1
SPECIFICATION OF STUDIED CHEMICALS

Chemical name	CAS No.	Molar mass ($g\ mol^{-1}$)	Mass fraction purity
Manganese sulphate	10034-96-5	169.02	≥ 0.980
Cobalt sulphate	10026-24-1	281.10	≥ 0.990
Nickel sulphate	10101-97-0	262.86	≥ 0.980
Copper sulphate	7758-99-8	249.68	≥ 0.990
Zinc sulphate	7446-20-0	287.54	≥ 0.999
Magnesium sulphate	10034-99-8	246.47	≥ 0.990
Ethylene glycol	107-21-1	62.07	≥ 0.999

which shows the isotropic nature of the membrane. The design of the apparatus and its experimental set up is shown in Fig. 1. The apparatus consists of a pyrex glass tube of 30 cm in length having a slight constriction in the middle with an internal diameter 1.858 cm where the plug of aluminum oxide is set up. This tube has two standard female joints B-24 at the ends. To the standard B-24 male joints are fixed the coiled platinum electrodes F and G. The ends of the electrodes are fused in glass tubes of diameter 5 mm, so that the electrode ends are insulated from the permeant. The lengths of these glass tubes are adjusted in such a way that when standard joints are kept in position, the electrodes touch the cross-sectional surface of the membrane. The main tube has two sides tubes H and K, bearing B-14 female standard joints D and E. Through the joint E a capillary tube, J, of length 20 cm and diameter 0.16 cm bent at 900 is connected to the side tube K. A graduated tube I of length about 50 cm and 1.0 cm in diameter is connected to the sides tube H through another standard joint D.

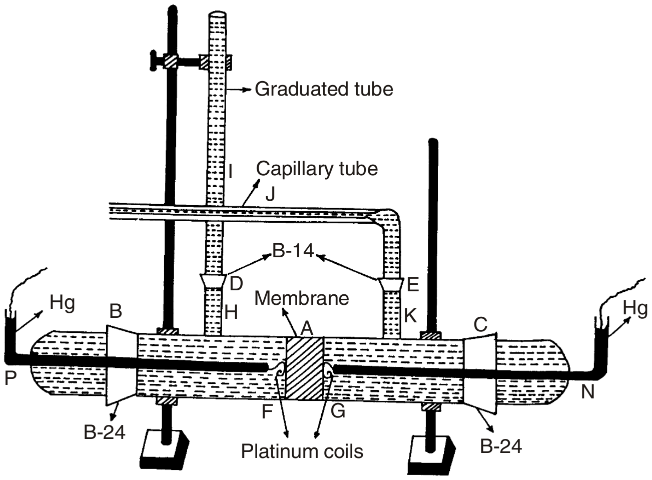

Fig. 1. Schematic set up of the apparatus

The experimental cell was filled with water and left overnight for equilibration of the membrane. The cell was then thoroughly washed with fresh distilled water under pressure gradient to ensure the thorough cleanliness. The apparatus was filled by adding conductivity water on one side of the membrane and then sucking it to the other side under a pressure gradient by mean of a vacuum pump. This ensured the complete filling of the capillaries of the membrane. Thus tubes J and I were then introduced and the apparatus suitably mounted inside the thermostat, where it was allowed to attain a constant temperature. The temperature was adjusted with the help of an electronic relay. In order to measure the hydrodynamic permeability, desired pressure difference was introduced across one side of the cell with the help of a pressure head. The system was kept in the thermostat for about 2 h to allow the experimental solution to attain the temperature of the thermostat. The rate of flow of liquid at desired pressure difference was measured by noting the time taken by the solution to move a certain distance through horizontal capillary. The flow time was recorded with the help of a stopwatch of least count 0.01 second. In this way the flow was recorded at different pressures.

RESULTS AND DISCUSSION

In the present study, the hydrodynamic permeabilties of some divalent transition metal sulphates *e.g.*, manganese sulphate, cobalt sulphate, nickel sulphate, copper sulphate, zinc sulphate and magnesium sulphate in binary aqueous mixture of 5 % ethylene glycol through an inorganic membrane of aluminum oxide have been determined. The permeability of any membrane depends upon the molecular size of the permeating fluid, the state of aggregation of the liquid, the number of hydrogen bonds *etc*. The hydrodynamic permeability of the permeating fluids through porous media, due to pressure gradient, varies exponentially [12] with temperature. The dependence of flow on the temperature is characterized in term of activation energy [13]. In order to obtain activation energy and hence free energy, the hydrodynamic permeabilities for different solutions of the transition metal sulphates *viz.*; manganese sulphate, cobalt sulphate, nickel sulphate, copper sulphate and zinc sulphate; and magnesium sulphate in 5 % (w/w) binary aqueous mixture of ethylene glycol have been determined at different temperatures (298.15, 303.15, 308.15, 313.15 and 318.15 K). The values of volume flow 'J_v' per unit area of the membrane, for the different solutions of transition metal sulphates and magnesium sulphate in 5 % (w/w) binary aqueous mixture of ethylene glycol are given in Table-2.The variation of volume flow 'J_v' with pressure difference (ΔP) for a particular solute in ternary system at different temperatures have been found to be linear. Sample plots of J_v *vs.* ΔP for manganese sulphate in 5 % (w/w) ethylene glycol + water at 303.15 K are shown in Fig. 2.

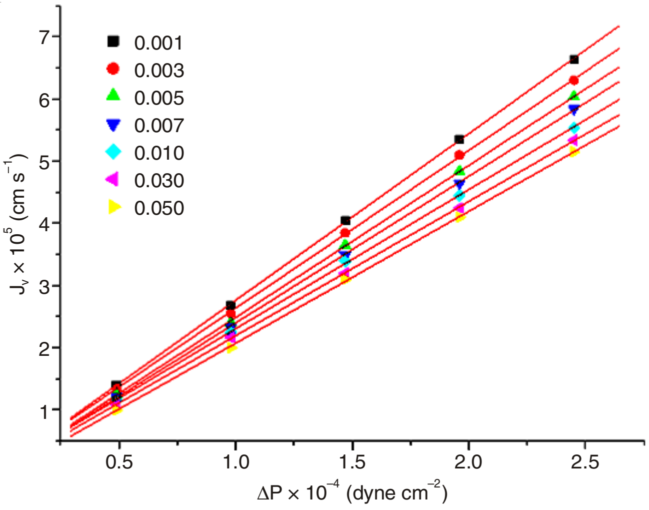

Fig. 2. Plot of J_v *vs.* ΔP for various concentrations of manganese sulphate in 5 % ethylene glycol + water mixture at 303.15 K

TABLE-2
RESULTANT VOLUME FLOW ($J_v \times 10^5$ cm s^{-1}) FOR DIFFERENT CONCENTRATIONS OF MANGANESE SULPHATE, COBALT SULPHATE, NICKEL SULPHATE, COPPER SULPHATE, ZINC SULPHATE AND MAGNESIUM SULPHATE IN 5 % (w/w) BINARY AQUEOUS MIXTURE OF ETHYLENE GLYCOL AT DIFFERENT TEMPERATURE

ΔP (× 10^{-4} dyne cm^{-2})	Molar concentration (mol kg^{-1})							Molar concentration (mol kg^{-1})						
	0.001	0.003	0.005	0.007	0.010	0.030	0.050	0.001	0.003	0.005	0.007	0.010	0.030	0.050
	Manganese sulphate							Cobalt sulphate						
	Temperature = 298.15 K							Temperature = 298.15 K						
0.49	1.35	1.25	1.21	1.16	1.12	1.08	0.90	1.35	1.28	1.23	1.18	1.13	1.08	1.03
0.98	2.50	2.40	2.25	2.20	2.15	2.10	1.90	2.60	2.45	2.35	2.30	2.25	2.15	2.07
1.47	3.85	3.60	3.45	3.30	3.15	3.05	2.90	3.85	3.70	3.56	3.40	3.25	3.13	3.00
1.96	5.10	4.80	4.55	4.40	4.20	4.00	3.85	5.10	4.85	4.70	4.50	4.33	4.15	3.95
2.45	6.30	5.95	5.70	5.50	5.15	5.05	4.82	6.32	6.06	5.83	5.55	5.35	5.13	4.90
	Temperature = 303.15 K							Temperature = 303.15 K						
0.49	1.40	1.35	1.26	1.21	1.15	1.08	1.00	1.37	1.30	1.25	1.19	1.15	1.10	1.05
0.98	2.68	2.55	2.40	2.34	2.25	2.17	2.00	2.66	2.51	2.42	2.25	2.20	2.10	2.03
1.47	4.05	3.85	3.65	3.50	3.40	3.20	3.10	4.00	3.85	3.63	3.50	3.35	3.20	3.10
1.96	5.35	5.10	4.84	4.65	4.45	4.25	4.10	5.36	5.10	4.80	4.65	4.45	4.26	4.10
2.45	6.64	6.30	6.04	5.84	5.54	5.34	5.15	6.66	6.32	6.00	5.75	5.52	5.30	5.10
	Temperature = 308.15 K							Temperature = 308.15 K						
0.49	1.45	1.40	1.35	1.30	1.26	1.18	1.10	1.45	1.40	1.35	1.30	1.25	1.20	1.15
0.98	2.80	2.65	2.50	2.40	2.30	2.20	2.10	2.80	2.70	2.55	2.40	2.27	2.18	2.10
1.47	4.20	4.00	3.85	3.65	3.51	3.40	3.25	4.45	4.25	4.05	3.90	3.70	3.55	3.40
1.96	5.50	5.35	5.08	4.85	4.60	4.50	4.00	5.58	5.30	5.10	4.85	4.65	4.40	4.25
2.45	6.90	6.55	6.30	6.05	5.80	5.55	5.35	6.95	6.60	6.30	6.05	5.80	5.50	5.32
	Temperature = 313.15 K							Temperature = 313.15 K						
0.49	1.50	1.45	1.10	1.35	1.30	1.25	1.20	1.50	1.45	1.14	1.36	1.25	1.20	1.15
0.98	2.93	2.80	2.70	2.50	2.40	230	2.20	2.95	2.80	2.70	2.50	2.40	2.29	2.15
1.47	4.95	4.75	4.00	3.82	3.65	3.50	3.35	4.45	4.25	4.03	3.83	3.65	3.50	3.35
1.96	5.80	5.60	5.30	5.10	4.85	4.65	4.50	5.85	5.60	5.30	5.00	4.85	4.65	4.40
2.45	7.30	7.00	6.65	6.35	6.02	5.80	5.55	7.30	7.00	6.60	6.30	6.05	5.80	5.65
	Temperature = 318.15 K							Temperature = 318.15 K						
0.49	1.57	1.50	1.45	1.41	1.33	1.28	1.23	1.60	1.50	1.45	1.40	1.36	1.22	1.17
0.98	3.08	2.95	2.80	2.65	2.50	2.35	2.25	3.10	2.88	2.75	2.65	2.50	2.40	2.25
1.47	4.70	4.45	4.25	4.00	3.77	2.65	3.50	4.70	4.55	4.25	4.05	3.85	3.65	3.50
1.96	6.20	5.85	5.60	5.30	5.10	4.80	4.60	6.20	5.85	5.60	5.35	5.15	4.80	4.60
2.45	7.70	7.30	7.00	6.70	6.30	6.00	5.75	7.70	7.30	7.00	6.76	6.35	6.00	5.76
	Nickel sulphate							Copper sulphate						
	Temperature =298.15 K							Temperature = 298.15 K						
0.49	1.16	1.10	1.05	1.00	0.95	0.92	0.86	1.25	1.21	1.17	1.13	1.08	1.00	0.92
0.98	2.25	2.10	2.00	1.83	1.80	1.73	1.65	2.46	2.36	2.25	2.15	2.05	1.97	1.85
1.47	3.40	3.22	3.05	2.93	2.85	2.70	2.55	3.70	3.52	3.35	3.25	3.10	3.00	2.85
1.96	4.50	4.25	4.08	3.87	3.75	3.60	3.42	4.90	4.70	4.45	4.30	4.12	3.95	3.75
2.45	5.57	5.35	5.10	4.87	4.72	4.47	4.26	6.10	5.80	5.55	5.35	5.10	4.90	4.70
	Temperature = 303.15 K							Temperature = 303.15 K						
0.49	1.20	1.15	1.10	1.05	1.00	0.95	0.90	1.30	1.25	1.21	1.16	1.10	1.03	0.94
0.98	2.20	2.15	2.00	1.85	1.82	1.75	1.68	2.54	2.41	2.27	2.20	2.10	2.00	1.90
1.47	3.50	3.25	30.8	2.92	2.80	2.72	2.55	3.85	3.64	3.50	3.35	3.18	3.05	2.87
1.96	4.60	4.30	4.10	3.90	3.80	3.60	3.40	5.12	4.83	4.65	4.45	4.20	4.05	3.85
2.45	5.70	5.39	5.14	4.90	4.75	4.50	4.30	6.37	6.00	5.80	5.55	5.25	5.02	4.78
	Temperature = 308.15 K							Temperature = 308.15 K						
0.49	1.25	1.20	1.15	1.10	1.05	1.00	0.95	1.35	1.30	1.25	1.20	1.15	1.08	1.03
0.98	2.34	2.28	2.20	2.08	2.00	1.90	1.80	2.65	2.50	2.40	2.35	2.20	2.10	2.00
1.47	3.56	3.28	3.20	2.08	2.00	1.90	1.80	4.00	3.82	3.65	3.52	3.40	3.20	3.02
1.96	4.65	4.45	4.25	4.15	4.95	3.85	3.70	5.30	5.05	4.85	4.65	4.50	4.25	4.00
2.45	5.80	5.52	5.35	5.15	4.95	4.75	4.60	6.55	6.30	6.02	5.80	5.57	5.25	4.95
	Temperature = 313.15 K							Temperature = 313.15 K						
0.49	1.28	1.22	1.18	1.12	1.08	1.02	0.97	1.40	1.35	1.30	1.25	1.20	1.15	1.08
0.98	2.45	2.35	2.20	2.15	2.00	1.95	1.87	2.77	2.65	2.50	2.40	2.30	2.20	2.10
1.47	3.70	3.55	3.35	3.20	3.10	2.95	2.85	4.20	4.00	3.82	3.65	3.52	3.35	3.20
1.96	4.90	4.70	4.45	4.25	4.10	3.92	3.75	5.55	5.30	5.05	4.85	4.65	6.40	4.25
2.45	6.05	5.82	5.55	5.35	5.18	4.90	4.65	6.90	6.60	6.30	6.05	5.80	5.50	5.26
	Temperature = 318.15 K							Temperature = 318.15 K						
0.49	1.35	1.30	1.25	1.20	1.15	1.10	1.05	1.50	1.45	1.40	1.35	1.25	1.20	1.15
0.98	2.55	2.40	2.35	2.25	2.15	2.10	2.00	2.95	2.80	2.70	2.55	2.45	5.30	2.20
1.47	3.85	3.65	3.50	3.40	3.25	3.15	3.00	4.45	4.25	4.00	3.80	3.65	3.50	3.35
1.96	5.10	4.87	4.65	4.50	4.30	4.13	4.00	5.85	5.65	5.30	5.05	4.85	4.65	4.45
2.45	6.37	6.08	5.80	5.60	5.38	5.12	4.95	7.30	7.00	6.65	6.30	6.00	5.75	5.50

Zinc sulphate								Magnesium sulphate						
Temperature =298.15 K								Temperature = 298.15 K						
0.49	1.20	1.15	1.10	1.05	1.00	0.95	0.90	1.21	1.17	1.12	1.07	1.02	0.96	0.88
2.30	2.20	2.10	2.00	1.10	1.00	0.95	0.90	2.30	2.20	2.15	2.08	2.00	1.85	1.75
1.47	2.30	2.20	2.10	2.00	1.95	1.90	1.50	3.50	3.35	3.20	3.10	2.95	2.75	2.60
1.96	3.50	3.35	3.20	3.05	2.90	2.75	2.60	4.68	4.45	4.25	4.10	3.80	3.70	3.50
2.45	5.60	5.55	5.30	5.05	4.80	4.50	4.25	5.80	5.50	5.30	5.10	4.90	4.60	4.35
Temperature = 303.15 K								Temperature = 303.15 K						
0.49	1.26	1.21	1.15	1.12	1.05	1.00	0.92	1.25	1.20	1.16	1.10	1.05	0.97	0.90
0.98	2.43	2.33	2.20	2.15	2.02	1.90	1.82	2.45	2.32	2.20	2.10	2.00	1.90	1.80
1.47	3.72	3.50	3.36	3.20	3.05	2.85	2.75	3.70	3.52	3.32	3.17	3.10	2.92	2.75
1.96	4.93	4.65	4.45	4.28	4.12	3.87	3.67	4.90	4.67	4.40	4.25	4.10	3.88	3.65
2.45	6.08	5.82	5.55	5.30	5.05	4.82	4.55	6.05	4.80	5.55	5.27	5.10	4.80	4.60
Temperature = 308.15 K								Temperature = 308.15 K						
0.49	1.30	1.25	1.20	1.15	1.10	1.05	0.95	1.25	1.20	1.15	1.10	1.05	1.00	0.95
0.98	2.55	2.40	2.30	2.20	2.10	2.00	1.90	2.55	2.40	2.30	2.20	2.15	2.00	1.90
1.47	3.85	3.65	3.50	3.30	3.16	3.00	2.80	3.85	3.65	3.50	3.35	3.20	3.07	2.90
1.96	5.10	4.80	4.60	4.40	4.20	4.00	3.75	5.12	4.82	4.60	4.37	4.20	4.00	3.80
2.45	6.30	6.00	5.75	5.50	5.25	4.95	4.55	6.35	6.10	5.75	5.50	5.25	5.05	4.80
Temperature = 313.15 K								Temperature = 313.15 K						
0.49	1.35	1.30	1.25	1.20	1.15	1.10	1.00	1.40	1.35	1.30	1.25	1.18	1.08	0.97
0.98	2.60	2.50	2.40	2.25	2.15	2.05	1.95	2.66	2.50	2.35	2.25	2.16	2.08	1.95
1.47	4.00	3.76	3.62	3.45	3.30	3.10	3.00	4.00	3.80	3.60	3.45	3.30	3.15	3.00
1.96	5.30	5.05	4.80	4.60	4.40	4.15	4.00	5.30	5.056	4.75	4.60	4.45	4.20	3.95
2.45	6.55	6.25	6.00	5.75	5.50	5.25	5.00	6.85	6.30	6.00	5.75	5.50	5.25	5.00
Temperature = 318.15 K								Temperature = 318.15 K						
0.49	1.40	1.35	1.30	1.25	1.20	1.10	1.05	1.45	1.41	1.34	1.28	1.20	1.10	1.00
0.98	2.80	2.70	2.55	2.44	2.30	2.20	2.06	2.75	2.65	2.50	2.40	2.25	2.15	2.07
1.47	4.25	4.05	3.85	3.70	3.50	3.30	3.15	4.20	4.00	3.80	3.65	3.50	3.30	3.20
1.96	5.70	5.35	5.10	4.80	4.65	4.35	4.13	5.55	5.25	5.00	4.80	4.75	4.40	4.20
2.45	5.95	6.60	6.35	6.05	5.75	5.40	5.10	6.95	6.60	6.25	6.00	5.75	5.50	5.25

Filtration coefficient or permeability coefficient (L_P): The thermodynamic relation for the volume flow (J_v), as a function of applied pressure difference (ΔP) and the osmotic pressure difference ($\Delta\pi$) across any membrane is given by the following expression.

$$J_v = L_P\Delta P - \sigma L_P\Delta\pi \qquad (1)$$

where the symbols have their usual significance.

It is convenient to determine the filtration coefficient, L_P, at $\Delta\pi = 0$ *i.e.* at equal concentrations of the solute on both the sides of membrane so that the above expression (eqn. 1) can be written as:

$$L_P = \left(\frac{J_v}{\Delta P}\right)_{\Delta\pi=0} \qquad (2)$$

The values of volume flow J_v, for the ternary solutions of transition metal sulphates and manganese sulphate at different temperatures are recorded in Table-2.

The above expression (eqn. 2) shows that the volume transported per unit area of the membrane per per unit time, should vary linearly with the hydrostatic pressure difference ΔP, across a membrane. The present experiments show that volume transported per unit time is linearly proportional to the pressure head for all the ternary solutions of divalent transition metal sulphates and magnesium sulphate at different temperatures (Fig. 2).

The values of permeability coefficient, L_P have been estimated from the slopes of linear plots of J_v *vs.* ΔP for the different ternary solutions of divalent transition metal sulphates and magnesium sulphate at different temperatures and these are recorded in Table-3.

The variation of L_P with concentration, for the different binary aqueous solution of divalent transition metal sulphates and magnesium sulphate, is linear.

The values of L_P have been obtained by the least squares method applied to the slopes of linear pots of J_v *vs.* ΔP and the corresponding values of permeability coefficient 'L_P' have been recorded in Table-3 for the present ternary system. The Compatibility of relation (eqn. 3) given below:

$$(J_v)_{\Delta\pi = 0} = L_P\Delta P \qquad (3)$$

with the Poissuille's law requires that

$$L_P = \pi\sum_{i=1}^{i=n} r_i^4 / 8\eta l \qquad (4)$$

Here r = radius of the ith capillary, n = number of capillaries or pores in membrane matrix, η = coefficient of viscosity of the permeating fluid and l = thickness of membrane. The variation of viscosity of fluid with temperature can be expressed as an activation process:

$$\eta = Ae^{-E_n}/RT \qquad (5)$$

where A = constant, E_n = activation energy.

Now substituting relation (eqn. 5) in (eqn. 4) and taking logarithm, it is found that:

$$\log L_P = K - E_n/RT \qquad (6)$$

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

The values of log L_P for the different ternary solutions at different temperatures are given in Table-4. According to relation (eqn. 6) when log L_P is plotted as a function of 1/T, a straight line should be obtained and the same has been found

TABLE-3
MECHANICAL FILTRATION COEFFICIENT (L_P, × 10^9 cm^3 $dyne^{-1}$ s^{-1}) FOR DIFFERENT CONCENTRATIONS OF MANGANESE SULPHATE, COBALT SULPHATE, NICKEL SULPHATE, COPPER SULPHATE, ZINC SULPHATE AND MAGNESIUM SULPHATE IN 5 % (w/w) BINARY AQUEOUS MIXTURES OF ETHYLENE GLYCOL AT DIFFERENT TEMPERATURE

Molar concentration (mol kg^{-1})	Temperature (K)				
	298.15	303.15	308.15	313.15	318.15
Manganese sulphate					
0.001	2.562	2.695	2.787	2.965	3.152
0.003	2.418	2.551	2.705	2.849	2.971
0.005	2.311	2.459	2.557	5.684	2.848
0.007	2.229	2.371	2.449	2.582	2.711
0.010	2.072	2.250	2.332	2.436	2.570
0.030	2.016	2.172	2.262	2.346	2.436
0.050	2.006	2.131	2.193	2.254	2.334
Cobalt sulphate					
0.001	2.549	2.721	2.824	2.971	3.135
0.003	2.451	2.588	2.664	2.848	2.986
0.005	2.367	2.344	2.551	2.660	2.859
0.007	2.242	2.361	2.449	2.537	2.750
0.010	2.156	2.252	2.353	2.469	2.542
0.030	2.070	2.164	2.217	2.569	2.451
0.050	1.971	2.084	2.150	2.264	2.363
Nickel sulphate					
0.001	2.268	2.316	2.338	2.457	2.580
0.003	2.182	2.178	2.215	2.367	2.465
0.005	2.086	2.086	2.141	2.562	2.336
0.007	2.004	1.998	2.84	2.164	2.264
0.010	1.945	1.943	1.998	2.111	2.162
0.030	1.838	1.834	1.937	1.994	2.064
0.050	1.756	1.746	1.885	1.893	2.008
Copper sulphate					
0.001	2.488	2.607	2.674	2.824	2.971
0.003	2.361	2.443	2.572	2.675	2.859
0.005	2.246	2.369	2.457	2.572	2.684
0.007	2.170	2.260	2.253	2.469	2.541
0.010	2.072	2.131	2.283	2.367	2.439
0.030	2.004	2.055	2.150	2.234	2.346
0.050	1.939	1.973	2.016	2.154	2.244
Zinc sulphate					
0.001	2.367	2.448	2.572	2.658	2.745
0.003	2.254	2.365	2.438	2.551	2.694
0.005	2.162	2.264	2.336	2.438	2.592
0.007	2.049	2.150	2.234	2.346	2.451
0.010	1.947	2.070	2.131	2.244	2.346
0.030	1.814	1.969	2.008	2.131	2.203
0.050	1.783	1.867	1.855	2.059	2.084
Magnesium sulphate					
0.001	2.369	2.469	2.617	2.692	2.828
0.003	2.276	2.367	2.463	2.552	2.660
0.005	2.143	2.250	2.356	2.418	2.525
0.007	2.066	2.150	2.278	2.326	2.426
0.010	1.959	2.090	2.141	2.240	2.377
0.030	1.913	1.995	2.070	2.143	2.264
0.050	1.781	1.895	1.967	2.061	2.178

TABLE-4
VALUE OF log L_P (cm^3 $dyne^{-1}$ s^{-1}) FOR DIFFERENT CONCENTRATIONS OF MANGANESE SULPHATE, COBALT SULPHATE, NICKEL SULPHATE, COPPER SULPHATE, ZINC SULPHATE AND MAGNESIUM SULPHATE in 5 % (w/w) BINARY AQUEOUS MIXTURES OF ETHYLENE GLYCOL AT DIFFERENT TEMPERATURE

Molar concentration (mol kg^{-1})	Temperature (K)				
	298.15	303.15	308.15	313.15	318.15
Manganese sulphate					
0.001	-8.591	-8.569	-8.555	-8.528	-8.501
0.003	-8.617	-8.593	-8.568	-8.545	-8.527
0.005	-8.636	-8.609	-8.592	-8.571	-8.545
0.007	-8.652	-8.625	-8.611	-8.588	-8.567
0.010	-8.684	-8.648	-8.632	-8.613	-8.590
0.030	-8.695	-8.663	-8.646	-8.630	-8.613
0.050	-8.698	-8.671	-8.659	-8.647	-8.632
Cobalt sulphate					
0.001	-8.694	-8.565	-8.549	-8.527	-8.504
0.003	-8.611	-8.587	-8.574	-8.545	-8.525
0.005	-8.625	-8.614	-8.611	-8.597	-8.561
0.007	-8.649	-8.627	-8.611	-8.597	-8.595
0.010	-8.666	-8.647	-8.628	-8.607	-8.595
0.030	-8.684	-8.665	-8.656	-8.590	-8.611
0.050	-8.705	-8.581	-8.668	-8.645	-8.627
Nickel sulphate					
0.001	-8.644	-8.635	-8.631	-8.610	-8.588
0.003	-8.661	-8.662	-8.655	-8.626	-8.608
0.005	-8.681	-8.681	-8.669	-8.647	-8.532
0.007	-8.698	-8.699	-8.681	-8.665	-8.645
0.010	-8.711	-8.712	-8.69	-8.676	-8.674
0.030	-8.736	-8.737	-8.713	-8.700	-8.685
0.050	-8.755	-8.758	-8.725	-8.723	-8.697
Copper sulphate					
0.001	-8.604	-8.584	-8.573	-8.549	-8.527
0.003	-8.537	-8.612	-8.590	-8.569	-8.544
0.005	-8.649	-8.625	-8.610	-8.590	-8.571
0.007	-8.663	-8.646	-8.647	-8.607	-8.595
0.010	-8.684	-8.671	-8.541	-8.626	-8.613
0.030	-8.698	-8.687	-8.668	-8.651	-8.630
0.050	-8.712	-8.705	-8.696	-8.667	-8.649
Zinc sulphate					
0.001	-8.626	-8.611	-8.590	-8.571	-8.561
0.003	-8.647	-8.626	-8.613	-8.593	-8.570
0.005	-8.665	-8.645	-8.632	-8.613	-8.586
0.007	-8.688	-8.668	-8.651	-8.630	-8.611
0.010	-8.711	-8.684	-8.671	-8.649	-8.630
0.030	-8.741	-8.706	-8.697	-8.671	-8.657
0.050	-8.749	-8.729	-8.732	-8.686	-8.681
Magnesium sulphate					
0.001	-8.625	-8.607	-8.582	-8.570	-8.549
0.003	-8.643	-8.626	-8.608	-8.593	-8.575
0.005	-8.669	-8.648	-8.628	-8.616	-8.598
0.007	-8.685	-8.668	-8.642	-8.633	-8.615
0.010	-8.708	-8.680	-8.669	-8.650	-8.624
0.030	-8.718	-8.700	-8.684	-8.669	-8.645
0.050	-8.749	-8.722	-8.706	-8.686	-8.662

to be true for the various solutions of divalent transition metal sulphates and magnesium sulphate in binary aqueous solutions of ethylene glycol. Sample plot of log L_P *vs.* 1/T for different concentrations of magnesium sulphate in 5 % ethylene glycol + water is given in Fig. 3.

The slope of straight line plot of log L_P *vs.* 1/T gives the value of activation energy (E_n). The E_n values have been obtained by applying the least square method to the linear plots of log L_P *vs.* 1/T. The values thus obtained, for different solutions of ternary systems, have been taken as an enthalpy ($E_n = \Delta H^*$) for the viscous flow of permeating fluid through

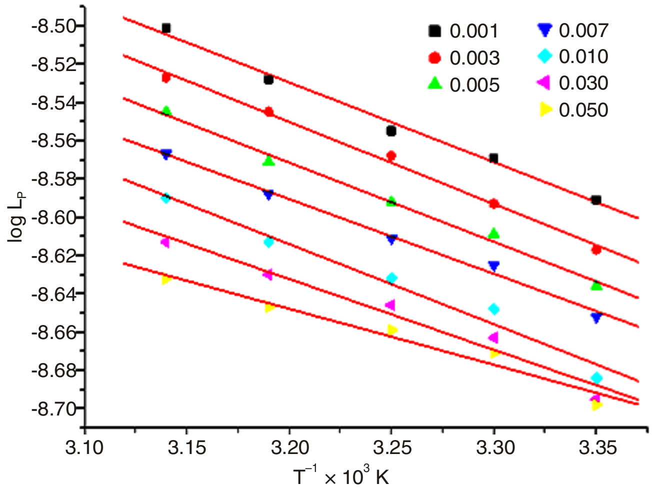

Fig. 3. Plot of log L_P *vs.* 1/T for mangnese sulphate in 5 % ethylene glycol + water

the inorganic membrane of aluminium oxide. The values of ΔH^*, for different ternary systems are recorded in Table-5.

Now using standard Eyring equation [12] given below:

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

where η = viscosity of a permeating fluid, N = Avogadro's number, h = Plank's constant, V = the molar volume of permeating fluid and ΔH^* = enthalpy of activation. The entropy of activation (ΔS^*) can be rearranged as follows:

$$\Delta S^* = \frac{\Delta H^*}{T} + R\log[N h / \nu\eta] \quad (8)$$

The value of densities, viscosities and molar volume for the different solution of electrolytes in ternary system are given in Table-6.

The values of ΔS^* for different ternary system obtained from the relation (eqn. 8) are also recorded in Table-5. It is clear from Table-5 that the values of ΔS^* are negative for the different solution of divalent transition metal sulphates and magnesium sulphate in 5 % (w/w) binary aqueous mixture of ethylene glycol at 303.15 K. The negative sign associated with ΔS^* shows that the hydrodynamic flow process, through the inorganic membrane of aluminum oxide, has the strong electrostatic interactions between the wall of the pores of the membrane. This may be attributed to the state of high order during the transport process of the electrolytes in ternary system through the inorganic membrane of aluminum oxide.

The values of ΔH^* and ΔS^*, thus calculated are related to ΔG^* by the following relation:

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

The values of ΔG^* for the ternary system calculated with the relation (eqn. 9) at 305.15 K, are also given in Table-5. It is now clear from Table-5 that the value of ΔG^* are positive for ternary system (mentioned above) at 303.15 K, thereby suggesting that the flow is not favoured across the inorganic membrane of aluminum oxide *i.e.* flow is non-spontaneous.

TABLE-5
VALUES OF THE ACTIVATION PARAMETERS (ΔH^*, ΔS^* AND ΔG^*) FOR MANGANESE SULPHATE, COBALT SULPHATE, NICKEL SULPHATE, COPPER SULPHATE, ZINC SULPHATE AND MAGNESIUM SULPHATE IN 5 % (w/w) BINARY AQUEOUS MIXTURES OF ETHYLENE GLYCOL

Molar concentration (mol kg^{-1})	$\Delta H^* \times 10^3$ (KJ mol^{-1})	$\Delta S^* \times 10^3$ (KJ mol^{-1})	$\Delta G^* \times 10^3$ (KJ mol^{-1})
Manganese sulphate			
0.001	-0.417	-22.776	6.904
0.003	-0.430	-22.826	6.919
0.005	-0.415	-22.783	6.906
0.007	-0.390	-22.707	6.883
0.010	-0.418	-22.808	6.914
0.030	-0.370	-22.695	6.880
0.050	-0.292	-22.473	6.812
Cobalt sulphate			
0.001	-0.410	-24.588	7.453
0.003	-0.403	-24.572	7.449
0.005	-0.378	-24.488	7.423
0.007	-0.362	-24.449	7.411
0.010	-0.387	-24.539	7.439
0.030	-0.421	-24.692	7.485
0.050	-0.362	-24.537	7.438
Nickel sulphate			
0.001	-0.259	-23.848	7.229
0.003	-0.270	-23.892	7.243
0.005	-0.250	-23.832	7.224
0.007	-0.264	-23.885	7.240
0.010	-0.209	-23.712	7.188
0.030	-0.262	-23.925	7.253
0.050	-0.284	-24.026	7.283
Copper sulphate			
0.001	-0.357	-23.988	7.272
0.003	-0.393	-24.114	7.310
0.005	-0.360	-24.012	7.279
0.007	-0.332	-23.926	7.253
0.010	-0.352	-24.001	7.276
0.030	-0.323	-23.946	7.259
0.050	-0.311	-24.038	7.287
Zinc sulphate			
0.001	-0.320	-24.491	7.424
0.003	-0.352	-24.482	7.421
0.005	-0.358	-24.515	7.431
0.007	-0.362	-24.515	7.431
0.010	-0.371	-24.574	7.449
0.030	-0.382	-24.655	7.474
0.050	-0.340	-24.550	7.442
Magnesium sulphate			
0.001	-0.355	-23.932	7.255
0.003	-0.317	-24.243	7.350
0.005	-0.326	-23.851	7.230
0.007	-0.368	-24.996	7.274
0.010	-0.372	-24.017	7.280
0.030	-0.383	-24.096	7.304
0.050	-0.394	-24.164	7.325

Conclusion

From the present studies, values of ΔS^* are found negative for the different solution of divalent transition metal sulphates and magnesium sulphate in 5 % (w/w) binary aqueous mixture of ethylene glycol at 303.15 K which shows that the hydrodynamic flow process, through the inorganic membrane

TABLE-6
DENSITIES (d), VISCOSITIES (η), MOLAR VOLUMES (V) FOR MANGANESE SULPHATE, COBALT SULPHATE, NICKEL SULPHATE, COPPER SULPHATE, ZINC SULPHATE AND MAGNESIUM SULPHATE IN 5 % (w/w) BINARY AQUEOUS MIXTURES OF ETHYLENE GLYCOL AT 303.15 K

Molar concentration (mol kg^{-1})	Densities (g cm^{-3})	Viscosities (Pa.s)	Molar volumes (cm^3 mol^{-1})
Manganese sulphate			
0.001	1.00196	0.8864	168.68
0.003	1.00227	0.8885	168.63
0.005	1.00255	0.8903	168.58
0.007	1.00204	0.8922	168.53
0.010	1.00327	0.8948	168.46
0.030	1.00607	0.9085	167.99
0.050	1.00878	0.9201	167.54
Cobalt sulphate			
0.001	1.00199	0.8860	280.54
0.003	1.00236	0.8881	280.44
0.005	1.00270	0.8899	280.34
0.007	1.00305	0.8918	280.24
0.010	1.00357	0.8742	280.10
0.030	1.00694	0.9068	279.29
0.050	1.01021	0.9170	279.20
Nickel sulphate			
0.001	1.00199	0.8862	262.34
0.003	1.00235	0.8883	262.24
0.005	1.00268	0.8901	262.16
0.007	1.00302	0.8920	262.07
0.010	1.00352	0.8946	261.94
0.030	1.00581	0.9071	261.08
0.050	1.01000	0.9172	260.26
Copper sulphate			
0.001	1.00203	0.8866	249.18
0.003	1.00242	0.8888	249.09
0.005	1.00276	0.8907	249.00
0.007	1.00312	0.8927	248.91
0.010	1.00367	0.8955	248.78
0.030	1.00720	0.9088	247.90
0.050	1.01058	0.9209	247.08
Zinc sulphate			
0.001	1.00201	0.8867	286.98
0.003	1.00239	0.889	286.87
0.005	1.00274	0.8908	286.77
0.007	1.00310	0.8928	286.67
0.010	1.00363	0.8956	286.52
0.030	1.00707	0.9098	285.54
0.050	1.01036	0.9213	284.61
Magnesium sulphate			
0.001	1.00195	0.8860	246.00
0.003	1.00223	0.8889	245.63
0.005	1.00248	0.8899	245.87
0.007	1.00274	0.8918	245.81
0.010	1.00312	0.8942	245.71
0.030	1.00561	0.9069	245.10
0.050	1.00800	0.9172	244.52

of aluminum oxide, has the strong electrostatic interactions between the wall of the pores of the membrane. This may be attributed to the state of high order during the transport process of the electrolytes in ternary system through the inorganic membrane of aluminum oxide. On the other hand values of ΔG^* are found positive for ternary system (mentioned above) at 303.15 K, thereby suggesting that the flow is not favoured across the inorganic membrane of aluminum oxide *i.e.* flow is non-spontaneous. In order words, it may be said that until an input force is applied across the inorganic membrane of aluminum oxide, the flow of permitting fluid cannot take place.

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