IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 9, Issue 1 Ver. I (Jan. 2016), PP 58-64
www.iosrjournals.org

Equivalent Pore Dimensions and Membrane Characterization parameters in Transport Phenomenon across Ion Exchange Membrane

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Abstract: *Transport studies across natural biological and artificial membranes are very important from experimental and theoretical point of view. Transport through bio membranes follows the principle of selective permeability and is very important to study drug membrane interactions. Non equilibrium thermodynamics plays an important role in studying transport phenomenon. In the present investigation membrane is prepared by mechanical compression of cation exchange resin Indion 236 with adhesive araldite. Equivalent pore radius for membrane for different concentrations of aqueous solutions of glucose and sucrose at different temperatures have been determined. The cation exchange membrane has been characterized in terms of membrane constant A/l. The present study tries to establish a relationship between equivalent pore radius ,concentration of solutesand temperature of study.*

I. Introduction

Studies of transport processes across natural and artificial membranes are of great importance both from experimental and theoretical point of view. The origin of transport phenomenon can be attributed to the urge of any system to move from non equilibrium to equilibrium state provided intensive state variables are constant at all time frames and have the same magnitude at all positions in system.

Ion Exchange membranes are highly charged artificial membranes with ionic groups, they include solid films, foils, discs, ribbons, tubes and plugs etc. Ion Exchange membranes involve the reversible interchange of ions between solid and liquid phase through Electrical double layer formed at the interface. Structurally the Ion Exchange membrane may be considered as the bundle of capillaries or channels having characteristic pore size and length. Chemically the matrix consists of an irregular, macromolecular, three dimensional network with charged ionic groups in its component polymer molecules. Mobile ions bearing the charge opposite to that born by the fixed ion are known as counter-ions, while those bearing the same charge are known as co - ions. Ion Exchange membranes are important as they can be used as simple models for the study of biological processes across biomembranes.

Transport phenomenon across membranes may be diffusion phenomenon or viscous phenomenon, transport across charged membranes can occur in a different manner executing anamolous osmosis instead of normal osmosis leading to transfer of solute in both directions[1-3].Transport phenomenon across a membrane depends on the nature of membrane[4-6] .Examination of relationship between Channel dimensions and frictional coefficients (staverman reflection coefficients) is very important for the understanding of transport phenomenon

The concept of equivalent pore radius has been used by many workers to characterize the behavior of membranes particularly biological membranes[7-11]Powerful treatments based upon irreversible thermodynamics have been applied to systems leading to new experimental evidences on equivalent pore radius.

There exist quantitative Hydrodynamic relationship between pore dimensions and friction as explained by various mathematical relations given by individual workers working on the subject. Fick's law can be used to describe free diffusion in one dimension in a solution and can be stated as

$J_0 = - D (\delta_c / \delta_x)$

WhereJ_0 is solute flux in moles per unit, c is concentration ,x is distance and D is the diffusion coefficient in free solution.Pepenheimer et.al.[12] used following equation derived by Ladenburg[15] to describe the friction of particles with in the membrane pores.

$g'/g^{0'}=1+2.4\alpha$

g' is friction exerted on solute molecule as a consequence of interaction with in the pore. α is ratio of the radius of solute to pore.

Pepenheimer also emphasized on the need of an additional factor for accounting the probability that a particle will actually enter the pore, as a particle could only enter the pore, if it does not strike with the rim.

Renkin [16] however preferred equation derived by Faxenon theoretical grounds as compared to Ladenberg's equation

$g^0/g = 1-2.104\,\alpha + 2.09\alpha^3 - 0.95\alpha^5$

Faxen's equation considered fluid to be in continuum, made up of small sphere molecules.Staverman in 1951[13] introduced reflection coefficient to describe osmotic properties of semipermeable membranes permitting restricted passage of solute.

II. Experimental

2.1 materials

2.1.1chemical reagents

Sucrose and Glucose of analytical grade and used as such after drying over P_2O_5 in a vacuum dessicator.

2.1.2 water

Water required for the preparation of solutions and for the calibration of Viscometer and Pycnometer was prepared by distilling twice in an all glass double distillation unit supplied by Systronics India Ltd. Specific conductance of water thus prepared was of the order of $10^{-6}ohm^{-1}cm^{-1}$.Water was stored in Borosilicate glass bottles.

2.1.3 cation exchange resin

Indion 236 from sd fine Chemicals India was used for the preparation of membrane.

2.2 Preperation of membrane

The cation exchange resin (Indion 236)was swollen in conductivity water and cased in the form of plug as described below 9 gm. of ion-exchange resin along with small amount of (5-7%)of an adhesive (araldite)was placed in a Pyrex glass assembly having constriction in the middle and compressed mechanically at the site of constriction with the help of mechanical device consisting of wooden rods having diameter slightly less than that of glass tube. The screws of the device were tightened and assembly was left as such for 24 hours for the complete setting of the plug. The thickness and diameter of the plug thus prepared were 2.29 cms and 1.398 cms respectively. The maximum variation in the permeability of the ion –exchange membrane , thus prepared for a period of one week was only of the order of 5%.

In order to know about the directional character of the membrane for the permeation of water the hydraulic permeability was measured in both the directions at $35^{\circ}C$ and the values were found to be same in both the directions, thereby indicating the isotropic character of the membrane.

2.3 apparatus

The apparatus consists of a pyrex glass tube of 24 cms. In length having a slight constriction in the middle with an internal diameter 1.398 cm, where the plug of cation exchange resin 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 side tubes H and K,bearing B-14 female standard joints D and E. Through the joint E a capillary tube J, of known diameter, bent at 90° of length 25 cm. is connected to the side tube K. A graduated tube I of about 30 cms in length and 1.0 cm. in diameter is connected to the side tube H, through another standard joint D.The design of apparatus and experimental set up is shown in "Fig"1

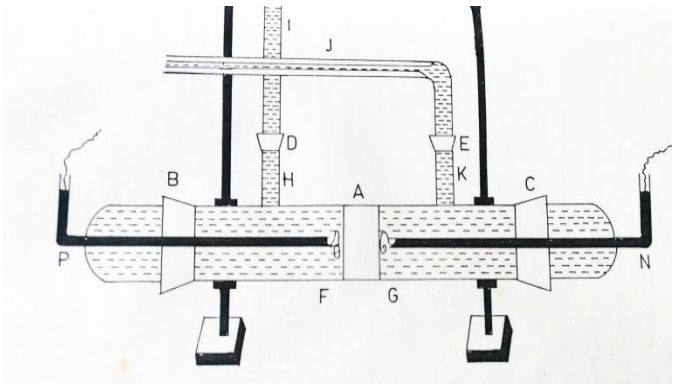

fig.1. schematic set up of the apparatus.

2.4 working procedure

The experimental cell was filled with water and left overnight for equilibration of the plug. The cell was then thoroughly washed with fresh distilled water under pressure gradient to ensure thorough cleanliness. The cell was then filled, by adding the solution under investigation on both sides of the membrane and left overnight. Next day the solution was thrown. The apparatus was then filled by adding the solution under investigation on one side of the membrane and then forcing it to the other side under the pressure gradient by vacuum pump. This ensures the complete filling of the capillaries of the membrane. The whole apparatus was then kept in air thermostat maintained at the desired temperature with in $\pm 0.05°C$. For the measurement of hydrodynamic permeability, desired pressure difference was applied across one side of the cell with the help of a pressure head.The system was kept in the thermostat for about two hours to allow the experimental solution to attain the temperature of the thermostat. At desired pressure difference, the rate of flow of liquid was measured by noting the time taken by the solution to move a certain distance i.e one cm. through horizontal capillary. Time of flow was recorded by using a stopwatch of least count 0.1s.The flow was recorded at different pressures and temperatures.

Conductance of the system and specific conductance was noted with the help of Digital conductivity meter. The conductivity cell consisted of two platinum electrodes fused with glass.Density of the solution is noted with pre calibrated Pycnometer and viscosity was measured with a suspended lebel type viscometer.

2.5 Sources of Error

The main source of error and factor responsible for affecting reproducibility of results is the incomplete wetting ofthe membrane, as rate of flow of liquid depends upon the actual number of capillaries transmitting the liquid. This was ensured by introducing the solution after evacuation of the apparatus and by preparing the solution from degassed water

III. Results And Discussion

3.1 membrane characterization

The thickness of the membrane was measured with the help of a cathetometer, measuring up to 0.001 cm. and thickness is found to be 2.29 cm. Diameter of the membrane was noted with the travelling microscope of 0.001 cm. sensitivity and found to be 1.398 cm.

The rate of permeation through the membrane ,under the influence of hydrostatic pressure depends upon the effective cross-sectional area. Determination of the effective cross-sectional area is difficult due to the complex geometry of the opening with in the membrane. It is however possible to determine the ratio A/l,so called membrane constant, in terms of which the permeant behavior of any membrane can be expressed quantitatively.

For a membrane having 'n' pores of equivalent radius 'r', the effective cross-sectional area 'A', through which permeation occursis $n\pi r^2$. The electrical conductance K of the membrane equilibrated with a permeant having specific conductance k is given by

$K = n\pi r^2 . k/l = (A/l).k$

So that the membrane constant is

$A/l = K/k$

This constant is characteristic parameter of the membrane and is independent of the permeating liquid as long as the interaction between the permeant and the membrane matrix is not strong enough to alter ϕ. values of membrane constant are fairly constant for different solutions as listed in table 1. and are in accordance with the findings of singh et.al.[14]. In other words, the membrane constant, A/l is a characteristic of membrane only and is independent of the nature of permeating liquid.

The equivalent pore radius can be evaluated from the equation

$$\left[\frac{J_v}{\Delta P}\right]_{\Delta\phi=0} = \frac{n\pi r^4}{8\acute{\eta} l} = \frac{n\pi r^2 r^2}{8\acute{\eta} l}$$

$$\left[\frac{J_v}{\Delta P}\right]_{\Delta\phi=0} = \frac{n\pi r^2}{l} \times \frac{r^2}{8\acute{\eta}}$$

$$r^2 = \left[\frac{8\acute{\eta}\left(\frac{J_v}{\Delta P}\right)\Delta\phi=0}{A/l}\right]$$

$$r = \sqrt[2]{\left[\frac{8\acute{\eta}\left(\frac{J_v}{\Delta P}\right)\Delta\phi=0}{A/l}\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.$$

where $\acute{\eta}$ is coefficient of viscosity of the permeating liquid, J_v the volume flow, ΔP the pressure difference of the permeant and $\Delta\phi$ the potential across the membrane.

The values of volume flow J_v , for different concentrations of glucose and sucrose in water at different pressure heads and different temperatures is given in Table II, further the value of viscosity coefficient and

density for various solutions are recorded in Table III.The equivalent pore radius evaluated from equation 1. for different solutions are listed in table IV.

It is evident from Table IV that the equivalent pore radius, in case of glucose and sucrose solutions at 308K , first decreases and then increases with increase of concentration of glucose and sucrose i.e a reversal has been observed. Further , at other temperatures i.e. at 313K and 318 K the equivalent pore radius continuously decreases with the increase of concentrations of sucrose in water. The reverse has been observed in case of glucose solution i.e the equivalent pore radius increases with increase in concentration of glucose.These changes in the pore radius with the change in concentrations of sucrose and glucose may be attributed to the change in the thickness of electrical double layer at solution membrane interface. In other words, the behavior of Sucrose and Glucose towards equivalent pore radius or electrical double layer, in case of present membrane is opposite to each other.

Table 1. Membrane characteristics for different solutions of Glucose and Sucrose at different Temperatures (ascertained from Hydrodynamic permeability data)

For glucose

Concentration $C\times10^2$mol l^{-1}	$K\times10^6 ohm^{-1}$	$k\times10^6 ohm^{-1}cm^{-1}$	A/l (cm)
	Glucose in Water temperature 308K		
0.099	8.45	65.00	0.13
0.29	8.90	69.00	0.13
0.49	9.20	71.00	0.13
0.69	9.40	67.85	0.14
0.99	9.10	70.00	0.13
2.96	9.65	74.20	0.13
4.92	11.56	82.60	0.14
6.91	11.28	99.00	0.11
	Temperature 313K		
0.099	8.70	67.00	0.13
0.29	9.10	70.10	0.13
0.49	9.43	72.50	0.13
0.69	9.90	76.40	0.13
0.99	9.70	81.00	0.12
2.96	10.00	76.90	0.13
4.92	11.00	84.60	0.13
6.91	12.00	92.30	0.13
	Temperature 318 K		
0.099	9.00	69.23	0.13
0.29	9.50	73.07	0.13
0.49	10.00	76.92	0.13
0.69	10.50	80.77	0.13
0.99	11.00	84.61	0.12
2.96	11.70	83.15	0.14
4.92	12.00	100.00	0.12
6.91	13.00	102.00	0.13

Table For sucrose

Concentration $C\times10^2$mol l^{-1}	$K\times10^6 ohm^{-1}$	$k\times10^6 ohm^{-1}cm^{-1}$	A/l (cm)
	Sucrose in Water temperature 308K		
0.099	12.45	95.80	0.13
0.29	12.76	98.20	0.13
0.49	13.75	105.80	0.13
0.69	14.88	114.50	0.14
0.99	15.08	116.00	0.13
2.96	16.77	119.80	0.14
4.92	16.32	125.60	0.13
6.91	17.03	131.00	0.13

	Temperature 313K		
0.099	12.80	98.46	0.13
0.29	13.00	100.00	0.13
0.49	14.00	107.69	0.13
0.69	15.50	119.23	0.13
0.99	16.00	133.33	0.12
2.96	17.00	121.42	0.14
4.92	17.00	130.76	0.13
6.91	18.00	138.46	0.13
	Temperature 318 K		
0.099	13.00	100.00	0.13
0.29	14.00	107.69	0.13
0.49	15.00	114.89	0.13
0.69	16.00	121.77	0.13
0.99	17.00	130.76	0.13
2.96	18.50	142.30	0.13
4.92	19.00	146.15	0.13
6.91	22.00	157.14	0.14

Table II

Hydrodynamic flow for different concentrations of Glucose and Sucrose in Water at different Temperatures

Pressure difference $\Delta P \times 10^{-4}$ Dyne cm^{-2}	$J_v \times 10^5$ Cmsec^{-1}							
Conc.(moll^{-1})	0.099	0.29	0.49	0.69	0.99	2.96	4.92	6.91
Temperature 308K	Glucose in Water							
3.9	3.69	3.54	3.44	3.20	5.05	5.49	5.83	7.19
3.4	3.25	3.10	2.90	2.75	4.39	4.81	4.99	6.43
2.9	2.75	2.60	2.55	2.35	3.68	4.18	4.32	5.43
2.4	2.30	2.15	2.05	2.00	3.05	3.45	3.65	4.55
1.9	2.00	1.75	1.60	1.40	2.50	2.74	2.86	3.56
Temperature 313 K								
3.9	3.75	4.17	4.45	5.60	6.52	6.00	6.48	6.95
3.4	3.20	3.29	3.75	4.85	6.00	5.33	5.73	5.82
2.9	2.30	3.00	3.21	4.10	4.90	4.45	4.79	5.30
2.4	2.40	2.56	2.62	3.27	4.11	3.65	4.07	4.32
1.9	1.80	2.00	2.10	2.99	3.17	2.75	2.88	3.55
Temperature 318 K								
3.9	6.80	8.60	13.10	14.20	12.30	15.10	20.20	21.00
3.4	6.00	7.90	10.00	12.30	10.20	12.60	17.50	18.70
2.9	4.80	6.30	8.40	10.50	8.60	10.40	15.00	15.80
2.4	4.20	5.00	7.00	8.70	7.10	8.90	12.30	12.90
1.9	2.40	4.20	4.60	5.50	4.10	7.04	7.90	9.02
Pressure difference $\Delta P \times 10^{-4}$ Dyne cm^{-2}	$J_v \times 10^5$ Cmsec^{-1}							
Conc.(moll^{-1})	0.099	0.29	0.49	0.69	0.99	2.96	4.92	6.91
Temperature 308K	Sucrose in Water							
3.9	4.22	3.95	3.79	3.33	3.94	5.07	6.43	6.66
3.4	3.52	3.48	3.36	2.89	3.29	4.54	5.32	5.56
2.9	3.10	2.90	2.86	2.50	2.78	3.79	4.55	4.97
2.4	2.51	2.41	2.43	1.97	2.36	3.06	3.71	4.10
1.9	1.97	1.70	1.87	1.63	1.84	2.57	3.04	3.21
Temperature 313 K								
3.9	6.20	5.60	3.90	3.47	2.56	1.96	1.34	1.15
3.4	5.27	4.79	3.35	2.85	2.26	1.60	1.20	1.07
2.9	4.72	4.25	2.90	2.56	1.93	1.40	1.05	0.78
2.4	3.85	3.50	2.27	2.10	1.54	1.15	0.88	0.70
1.9	3.12	2.96	1.92	1.67	1.31	1.03	0.69	0.55
Temperature 318 K								
3.9	7.56	7.12	5.93	4.00	3.48	2.10	1.96	1.65
3.4	5.95	5.83	5.22	3.30	2.93	1.87	1.69	1.45

2.9	5.60	4.42	4.17	2.82	2.33	1.55	1.35	1.25
2.4	4.62	4.05	3.65	2.40	2.05	1.39	1.25	0.90
1.9	3.79	3.20	2.25	1.84	1.65	1.00	0.96	0.85

Table III

Density, Viscosity and Equivalent Pore radius for Glucose and Sucrose in water at different Temperatures

Concentration $C\times10^2$ moll^{-1}	Density D gcm^{-3}	Viscosity $\dot{\eta}$	Pore radius $r \times 10^7$ cm
Glucose in Water Temperature 308K d° =0.9941 $\dot{\eta}^\circ$ =0.7225			
0.099	0.99411	0.72350	0.35
0.29	0.99450	0.72701	0.39
0.49	0.99479	0.72768	0.42
0.99	0.99502	0.72829	0.58
2.96	0.99518	0.73270	0.64
6.91	0.99878	0.73930	0.97
Temperature 313K d° =0.9922 $\dot{\eta}^\circ$ =0.6560			
0.099	0.99221	0.66320	0.41
0.29	0.99229	0.66571	0.45
0.49	0.99238	0.66849	0.49
0.99	0.99270	0.67501	0.57
2.96	0.99469	0.67939	0.67
6.91	0.99721	0.68578	0.74
Temperature 318K d° =0.99025 $\dot{\eta}^\circ$ =0.5960			
0.099	0.99030	0.59761	0.63
0.29	0.99039	0.60040	0.83
0.49	0.99061	0.60189	1.06
0.99	0.99069	0.60538	-
2.96	0.99248	0.61901	1.36
6.91	0.99712	0.62710	-
Concentration $C\times10^2$ moll^{-1}	Density D gcm^{-3}	Viscosity $\dot{\eta}$	Pore radius $r \times 10^7$ cm
Sucrose in Water Temperature 308K d° =0.9941 $\dot{\eta}^\circ$ =0.7225			
0.099	0.99440	0.73109	0.51
0.29	0.99469	0.73288	0.45
0.49	0.99501	0.73390	-
0.99	0.99708	0.73879	0.42
2.96	0.99871	0.74010	0.56
6.91	1.01109	0.75292	0.79
Temperature 313K d° =0.9922 $\dot{\eta}^\circ$ =0.6560			
0.099	0.99231	0.66810	0.68
0.29	0.99260	0.66989	0.58
0.49	0.99279	0.67161	0.41
0.99	0.99361	0.67701	0.28
2.96	0.99630	0.68149	0.21
6.91	1.00122	0.69349	0.14
Temperature 318K d° =0.99025 $\dot{\eta}^\circ$ =0.5960			
0.099	0.99030	0.61160	0.73
0.29	0.99051	0.61549	0.63
0.49	0.99119	0.61910	0.59
0.99	0.99172	0.62288	0.86
2.96	0.99410	0.62731	0.56
6.91	0.99958	0.63601	0.45

IV. Conclusion

In the present investigation cation exchange membrane has been prepared with Indion- 236.Transport studies viz. hydrodynamic permeabilities of aqueous solutions of glucose and sucrose in water across the membrane at various concentrations and different temperatures have been carried out. The membrane was characterized in terms of membrane constant A/l.As suggested by experimental data the membrane constant has been found to be fairly constant for glucose and sucrose solutions, indicating that the membrane constant is characteristic of the membrane only and is independent of the nature of the permeating liquid. Equivalent pore radius however changes with temperature , concentration and nature of the solute. It can be concluded that equivalent pore radius depends on the thickness of the electrical double layer formed at the solution membrane interface. The thickness of electrical double layer formed depends upon the type of solute, concentration of the solute and and temperature of the system.

The finding can be applied to biological systems, when bio membranes exhibit different pore radius for different transport events occurring on the bio membrane drug interface.

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