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STUDY OF TRANSPORT PROPERTIES OF AQUEOUS SOLUTIONS OF 1,4-DIOXANE AS A FUNCTION OF TEMPERATURE.

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ABSTRACT Aqueous solutions of different concentrations (10%, 20% and 30%) of 1,4-dioxane were prepared and transported through anisotropic cellulose acetate membrane over a range of temperature (298.15K, 303.15K and 308.15K) so as to study the effect of temperature and concentration on various transport properties of solutions such as hydrodynamic flow (J_v), permeability coefficient (L_p) and frictional coefficient (F_{wm}). The cellulose acetate membrane used in the present investigation was prepared by impregnating mixed solution of cellulose acetate in acetone and potassium bromide (KBr) in water through G_2 sintered disc. The membrane properties were evaluated in term of number of pores and equivalent pore radius. The membrane showed good mechanical property with the membrane tensile strength and can acts as an efficient ultrafiltration composite membrane. The effect of pressure difference on the different transport properties such as hydrodynamic flow (J_v), permeability coefficient (L_p) and frictional coefficient (F_{wm}) was also studied.

KEYWORDS : 1, 4-dioxane, cellulose acetate membrane, aqueous solutions, temperature, pressure difference.

1. INTRODUCTION

Membrane technology have found greater acceptance in recent years and is rapidly gaining recognition for its flexibility and efficiency. The main advantage of membrane technology is that it works without the addition of chemicals and with relatively low energy use. With the advancement of membrane based separation technology, separation of specific molecules present in the liquids can be carried out by using membranes of different pore size and shape [1-3]. Orchestrating pore size of polymeric membranes is therefore important to prepare specific membrane for specific application [4]. Various physiological processes in plants and animals are irreversible and involve transport through membranes. The principal function of organisms such as exchange of matter and energy also occurs through membranes. Two basic processes of life viz photosynthesis and respiration take place in membranous organelles of chloroplast and mitochondria respectively. Membranes are now widely used for water treatment [5-7], virus and bacteria filtration, oil/water emulsion separation [8-10], processing of food substances and beverages [11] and demineralization of water by reverse osmosis [12-13]. Nanoporous membranes have received great attention in the field water desalination, biosensing and chemical separations. There have been numerous studies for separartion of biomolecules and analytes based on charge selectivity. It has been demonstrated that proteins can be separated by applying potentials across conductive alumina membranes. Membranes are increasingly being integrated in bioreactors which are a real alternative technology for the treatment of waste water and industrial effluents. Inspite of the large number of benefits, membrane involving processes are associated with the problem of membrane fouling which occurs due to the attached or adsorbed foulant on surface of the membrane sheet or inside the pores which are initially contained in the feed solution thereby decreasing the saparation efficiency of the membrane involving process. Fouling can be irreversible or reversible fouling. An irreversible fouling has a great affinity towards the membrane surface whereas the reversible fouling has less affinity towards the membrane surface and have low concentration of foulant on the vicinity of membrane surface [14-17]. Membrane fouling found in membrane processes involving aqueous application is called biofouling which is caused by the bacterial adhesion [18-19]. The phenomena of biofouling can be reversed by various physical and chemical treatments [20-21]. However, physical treatment solely is insufficient to recover the membrane's performance and the chemical treatment possibly damages the membrane's material [22-25].

2. Experimental

2.1 Material used

Cellulose acetate, acetone, potassium Bromide (KBr), distilled water and 1,4-dioxane were used as material during experimental work.

2.2 Membrane

Cellulose acetate membrane used in the study of transport properties of solutions was prepared by dissolving cellulose acetate in acetone and mixed up with water to which potassium bromide (KBr) had been added. The materials were taken in the proportion 22.2:66.7:10:1.1 respectively. The cellulose solution was finally impregnated into a previously washed and dried sintered G_2 disc under vacuum at 0-0.5 ^{0}C. The membrane prepared in this way was anisotropic and the flow would show a significant change on the reversal of direction of applied force and hence to avoid this all the flow studies were carried out in the direction of impregnation of cellulose acetate solution.

2.3 Apparatus

The apparatus used was made up of pyrex glass tube of length 20cm and diameter 3.0×10^{-2} cm with sintered disc of porosity G_2 in the middle which was impregnated with cellulose acetate solution. The tube had two standard female B-24 joints at each end which were closed. The main pyrex tube had two side tubes having female B-14 joints to which a capillary tube 'C' and pressure head 'H' were connected. The pressure head used to maintain pressure difference was attached to the side tube through a polythene tube having standard male B-14 joint. The whole apparatus was kept in air thermostat to maintain the temperature of the system.

3. RESULTS AND DISCUSSION

3.1. Determination of hydrodynamic permeability (Jv) and permeability coefficient (L_p)

According to thermodynamics of irreversible processes [26,27] the dissipation function [28], for the transport processes of liquids through a membrane under the influence of pressure difference (ΔP) and concentration gradient (Δπ) can be written as:

$$\Phi = J_v \Delta P + J_D \Delta \pi \qquad (1)$$

where 'J_v' is the volume flux per unit area of the membrane, 'J_D' is the diffusional flow, 'ΔP' is hydrostatic pressure difference and 'Δπ' is difference in concentration across the membrane. The linear phenomenological equations relating to flow and forces are given below:

$$J_v = L_p \Delta P + L_{pd} \Delta \pi \qquad (2)$$

$$J_D = L_{dp} \Delta P + L_d \Delta \pi \qquad (3)$$

Where, $\Delta \pi = RT\Delta C$

According to Onsagar's reciprocity relations;

$$L_{pd} = L_{dp} \qquad (4)$$

Where, 'L_p' and ' L_d'are the mechanical coefficients of filtration and diffusion respectively and 'L_{pd}' and 'L_{dp}' are the phenomenological coefficients.

When the concentration of solute is same on both sides of the membrane i.e., Δπ =0 then hydrodynamic permeability (Jv) and permeability coefficient (L_p) are related to one another by the relation as:

$J_v = L_P \Delta P$ (5)

Where 'L_P' is the permeability coefficient or simply permeability of the membrane for the liquids and it represents the velocity of fluid per unit pressure difference for the unit cross-sectional area of the membrane. The values of 'L_P' can be estimated from the linear plots of J_v versus ΔP for aqueous solutions of 1,4-dioxane.

The hydrodynamic permeability (Jv) of the solution through the membrane can be estimated by using the following relation as:

$J_v = \pi r^2 x / \pi R^2 t$ (6)

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

3.2. Determination of frictional coefficient (F_{wm})

Frictional coefficient (F_{wm}) of the transport processes across membrane was studied by Kedem and Katchalsky [28]. The explicit treatment of frictional forces may be approached by considering the simple case of water filtration through the membrane. If pure water is placed on both sides of the membrane, then the driving force is balanced by mechanical filtration force between water and the membrane matrix. Under the condition of steady flow, 'X_{wm}' is given as:

$X_{wm} = F_{wm} (V_w - V_m)$ (7)

Where, 'F_{wm}' is the coefficient of friction between solution and the membrane and it is a measure of resistance offered by the membrane to the solution.

Under the simple use of translation of thermodynamic coefficient into frictional coefficient, the permeability coefficient (L_P) can be related to the frictional coefficient (F_{wm}) by the relation as:

$L_P = \Phi_w V_w / F_{wm} \delta$ (8)

Where 'V_w' is the molar volume of water and 'Φ_w' is the water content of the membrane and is expressed as the volume fraction of the total membrane volume and is numerically equal to the fraction of membrane surface available for permeation and its value was 0.9974 in case of cellulose acetate membrane, 'δ' is the thickness of membrane and its value is 0.0042×10^{-3} m in the given case.

The values of hydrodynamic permeability (J_v), permeability coefficient (L_P) and frictional coefficient (F_{wm}) obtained by using equations (5), (6) and (8) for the aqueous solutions of different concentrations of 1,4-dioxane across anisotropic cellulose acetate membrane at different temperatures are indicated in Tables 1-9 as below:

Table 1: Hydrodynamic permeability (J_v), permeability coefficient (L_P) and frictional coefficient (F_{wm}) data for 10% aqueous solution of 1,4-dioxane at different pressure difference across anisotropic cellulose acetate membrane.

298.15K

Pressure difference $\Delta P\times10^3$(Nm^{-2})	Hydrodynamic permeability $J_v\times10^{-4}$(ms^{-1})	Permeability coefficient $L_P\times10^{-7}$(m^{3}N^{-1}s^{-1})	Frictional coefficient $F_{wm}\times10^8$(mNmol^{-1}s)
3.5	6.24	5.31	8.34
4.0	7.89	5.88	7.25
4.5	9.61	6.36	6.70
5.0	11.26	6.71	6.35
5.5	12.84	6.96	6.13

Table 2: Hydrodynamic permeability (J_v), permeability coefficient (L_P) and frictional coefficient (F_{wm}) data for 10% aqueous solution of 1,4-dioxane at different pressure difference across anisotropic cellulose acetate membrane

303.15K

Pressure difference $\Delta P\times10^3$(Nm^{-2})	Hydrodynamic permeability $J_v\times10^{-4}$(ms^{-1})	Permeability coefficient $L_P\times10^{-7}$(m^{3}N^{-1}s^{-1})	Frictional coefficient $F_{wm}\times10^8$(mNmol^{-1}s)
3.5	7.37	6.38	6.68
4.0	8.97	6.79	6.28
4.5	10.57	7.11	5.99
5.0	12.20	7.39	5.77
5.5	13.84	7.62	5.59

Table 3: Hydrodynamic permeability (J_v), permeability coefficient (L_P) and frictional coefficient (F_{wm}) data for 10% aqueous solution of 1,4-dioxane at different pressure difference across anisotropic cellulose acetate membrane.

308.15K

Pressure difference $\Delta P\times10^3$(Nm^{-2})	Hydrodynamic permeability $J_v\times10^{-4}$(ms^{-1})	Permeability coefficient $L_P\times10^{-7}$(m^{3}N^{-1}s^{-1})	Frictional coefficient $F_{wm}\times10^8$(mNmol^{-1}s)
3.5	8.52	7.49	5.69
4.0	9.84	7.57	5.63
4.5	11.22	7.67	5.56
5.0	12.87	8.22	5.38
5.5	14.59	8.98	4.75

Table 4: Hydrodynamic permeability (J_v), permeability coefficient (L_P) and frictional coefficient (F_{wm}) data for 20% aqueous solution of 1,4-dioxane at different pressure difference across anisotropic cellulose acetate membrane.

298.15K

Pressure difference $\Delta P\times10^3$(Nm^{-2})	Hydrodynamic permeability $J_v\times10^{-4}$(ms^{-1})	Permeability coefficient $L_P\times10^{-7}$(m^{3}N^{-1}s^{-1})	Frictional coefficient $F_{wm}\times10^8$(mNmol^{-1}s)
3.5	5.22	4.43	9.60
4.0	6.71	4.99	8.54
4.5	8.34	5.52	7.72
5.0	9.96	5.94	7.17
5.5	11.68	6.33	6.73

Table 5: Hydrodynamic permeability (J_v), permeability coefficient (L_P) and frictional coefficient (F_{wm}) data for 20% aqueous solution of 1,4-dioxane at different pressure difference across anisotropic cellulose acetate membrane.

303.15K

Pressure difference $\Delta P\times10^3$(Nm^{-2})	Hydrodynamic permeability $J_v\times10^{-4}$(ms^{-1})	Permeability coefficient $L_P\times10^{-7}$(m^{3}N^{-1}s^{-1})	Frictional coefficient $F_{wm}\times10^8$(mNmol^{-1}s)
3.5	6.11	5.28	8.07
4.0	7.62	5.77	7.39
4.5	9.21	6.20	6.88
5.0	10.75	6.52	6.54
5.5	12.57	6.93	6.15

Table 6: Hydrodynamic permeability (J_v), permeability coefficient (L_P) and frictional coefficient (F_{wm}) data for 20% aqueous solution of 1,4-dioxane at different pressure difference across anisotropic cellulose acetate membrane.

308.15K

Pressure difference $\Delta P\times10^3$(Nm^{-2})	Hydrodynamic permeability $J_v\times10^{-4}$(ms^{-1})	Permeability coefficient $L_P\times10^{-7}$(m^{3}N^{-1}s^{-1})	Frictional coefficient $F_{wm}\times10^8$(mNmol^{-1}s)
3.5	7.21	6.34	6.72
4.0	8.76	6.75	6.32
4.5	10.35	7.08	6.02
5.0	11.92	7.34	5.81
5.5	13.57	7.60	5.62

Table 7: Hydrodynamic permeability (J_v), permeability coefficient (L_P) and frictional coefficient (F_{wm}) data for 30% aqueous solution of 1,4-dioxane at different pressure difference across anisotropic cellulose acetate membrane.

298.15K

Pressure difference $\Delta P\times10^3$(Nm^{-2})	Hydrodynamic permeability $J_v\times10^{-4}$(ms^{-1})	Permeability coefficient $L_P\times10^{-7}$(m^{3}N^{-1}s^{-1})	Frictional coefficient $F_{wm}\times10^8$(mNmol^{-1}s)
3.5	4.63	3.94	10.82
4.0	6.13	4.57	9.33
4.5	7.75	5.13	8.31
5.0	9.43	5.62	7.58
5.5	11.18	6.06	7.03

Table 8: Hydrodynamic permeability (J_v), permeability coefficient (L_P) and frictional coefficient (F_{wm}) data for 30% aqueous solution of 1,4-dioxane at different pressure difference across anisotropic cellulose acetate membrane.

303.15K

Pressure difference $\Delta P \times 10^3 (Nm^{-2})$	Hydrodynamic permeability $J_v \times 10^{-4} (ms^{-1})$	Permeability coefficient $L_P \times 10^{-7} (m^3 N^{-1} s^{-1})$	Frictional coefficient $F_{wm} \times 10^8 (mNmol^{-1} s)$
3.5	6.10	5.28	8.07
4.0	7.62	5.77	7.38
4.5	9.13	6.15	6.93
5.0	10.65	6.45	6.60
5.5	12.18	6.71	6.35

Table 9: Hydrodynamic permeability (J_v), permeability coefficient (L_P) and frictional coefficient (F_{wm}) data for 30% aqueous solution of 1,4-dioxane at different pressure difference across anisotropic cellulose acetate membrane.

308.15K

Pressure difference ΔP×103(Nm-2)	Hydrodynamic permeability Jv ×10-4(ms-1)	Permeability coefficient LP×10-7(m3N-1s-1)	Frictional coefficient Fwm×108(mNmol-1s)
3.5	7.20	6.34	6.72
4.0	8.73	6.72	6.34
4.5	10.25	7.02	6.07
5.0	11.48	7.07	6.02
5.5	13.40	8.25	5.15

CONCLUSION

The study of data obtained showed that hydrodynamic permeability (J_v) increases with increase in pressure in all cases, however it deceases with increase in concentration of the solution which is in conformity to the viscosity changes. Whereas the value of permeability coefficient (L_P), decreases with increase in concentration of the solution which is in accordance with the fact that permeability is inversely proportional to the viscosity of the liquids. The value of frictional coefficient (F_{wm}), increases with increase in concentration of the solutions in all cases, indicating that solution-membrane interactions increases with increase in concentrations and hence with the viscosity of the medium. Further it has also been found that the values of hydrodynamic permeability (J_v) and permeability coefficient (L_P) increases with increase in temperature of the solution, whereas the value of frictional coefficient (F_{wm}) decreases with increase in temperature due to decrease in viscosity of the solution.

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