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Preparation and Characterization of 18-Crown-6 Modified Cellulose Acetate Membrane in Uni-Univalent Aqueous Electrolyte Solutions

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In present study, a cellulose acetate/18-crown-6 blend membrane (selective for K^+ ions) was prepared by the solvent vapourization method. The surface morphology of the modified membrane was characterized by scanning electron microscopy (SEM) analysis, which indicate the smooth and homogeneous membrane surface. The effect of water and electrolyte (KCl and NaCl) concentration on the rate of water sorption and porosity was explained on the basis of physico-chemical parameters *i.e.* water content and water activity of the membrane phase. The variation of ionic transport number with respect to water activity, *i.e.* $[dt^mK^+/da^m_w > dt^mNa^+/da^m_w]$ has been observed in the present system. The transport of ions under concentration gradient in term of permeability, flow and flux was estimated by membrane/solution conductance-time data. The variations of permeability, flux and flow values with respect to time for K^+ and Na^+ ions were found to be different. Membrane water activity (a^m_w) decreases with the increase of external electrolyte concentration. The effective fixed charge density of the membrane increases with increase of external electrolyte concentration. Permselectivity parameter of the membrane in both cases decline with increase of external electrolyte concentration.

Keywords: Water content, Water activity, Ionic transport number, Effective fixed charge density, Permselctivity.

INTRODUCTION

Membrane technology is more important than the other separation processes due to consumption of low energy, easy scale-up, less or no use of chemicals and no harmful byproduct formation [1]. Membrane processes cover a group of separation processes in which the characteristics of a membrane (porosity, selectivity, electric charge) are used to separate the components of a solution. The characteristics of membranes like simplicity, high efficiency, selectivity, low energy consumption and good stability make membranes important component in various chemical industries for the separation process [2,3]. Today, a membrane with high selective separation efficiency, good adsorption ability and high antifouling property for the industrial use and desalinating plant to separate ions still require.

Polymeric membranes are one of the fastest growing research areas both in academic and in industrial scales. Cellulose is one of the best materials for constructing the membranes and the most abundant renewable organic resource. The cellulose acetate, cellulose acetate butyrate and cellulose acetate propionate are the most common commercial cellulose esters which are widely used in the manufacture of membranes [4]. Among all cellulose derivatives, cellulose acetate is one of the most suitable membrane materials due to their high selectivity, high permeability, controlling pore size, high hydrophilicity, cost effective, moderate salt rejection and non-toxic in nature [5]. Cellulose acetate being desalted in nature is responsible for the removal of salt [6]. The cellulose acetate is a biodegradable and biocompatible polymer and significantly useful for the environmental and sustainable development.

The hydrophilic nature of cellulose acetate attempt good fouling property. Although, cellulose acetate membrane is not applicable for the more aggressive cleaning, because it has low oxidation, poor mechanical strength and low chemical resistance, then the modification of the cellulose acetate was suited to enhances the properties of the membrane [7].

Polymer blends are more effective technique to modify the membrane characteristic properties and provide a novel material which display new properties due to appropriate mixing of two component with their distinct characterstics. The blending of cellulose acetate and crown ether (18-crown-6) influence the structural modification of the membrane surface and also influences the efficiency and selectivity of the metal ion transport.

Crown ether is macrocyclic compounds which are capable to select and bind metal cationic species [8]. The binding of crown ether compound to cationic species is due to ion dipole interaction of the positively charged metal ion with negatively charged oxygen atom present in crown ether ring [9]. Generally, the complexation itself not selective for the specific ion but crown ether can form the more stable complex having similar diameter to the open cavity of the crown ether. The size of crown ether cavity is approximately 2.8 Å, which is similar to the size of K^+ ion (2.76 Å). Therefore, the potassium ion easily fit in the crown ether cavity and form the stable complex [10]. The specificity of the interaction with the metal cation makes these compounds are most beneficial for preparation of noble material as metal ion catalyst, molecular imprinting compound, chirality inducing reagents, ion exchange membrane, selective solvent separation, selective membrane transport, ion-selective membrane for sensors, *etc.* [11].

The crown ether (18-crown-6) has both hydrophilic and hydrophobic groups was co-mixed with cellulose acetate *via* hydrogen bonding between the hydroxyl groups of cellulose acetate and the oxygen groups of the crown ethers. One of the characteristic parameters of membrane *i.e.* hydrophilicity which help to attain higher water flux with lower resistant to foulants due to hydration layer develop on the membrane surface which inhibit the non-specific interaction between foulants and the surface of the membrane [12-14]. The surface hydrophobicity is responsible for antifouling property, since good hydrophobicity allow to the membrane a low apparent surface free energy and reduce the adhesion strength of foulants onto the membrane surface, which is responsible for easily removable of foulants [15].

Although among these advantages, cellulose acetate/18-crown-6 membrane are more susceptible to improve the degree of hydrophobicity in order to diminishes the fouling behaviour of membrane, adsorption behaviour, permeability and selectivity in ion separation. Due to such huge applicability, one can consider to improve the characterization and optimization of membrane in order to prepare cellulose acetate/18-crown-6 blended membrane by solvent vapourization method.

In present work, the transport behaviour of Na^+ and K^+ metal ions from the aqueous electrolytic solutions of (NaCl, KCl) by cellulose acetate/18-crown-6 membrane. Transport study has been carried out with the help of conductance measurement. Kinetic studies and membrane morphology (SEM) were established by the water content measurement in the term of flux of ions and porosity of the membrane.

EXPERIMENTAL

Cellulose acetate (acetyl content consisted of 53.5 to 54.5%, BDH chemical Ltd., England), crown ether 18-crown-6 (HPLC, India) as the ion carrier and acetone (Qualigens Fine chemicals, India) as solvent were used for membrane formation. Sodium chloride (AR Grade, SDFCL, India), potassium chloride (GR, Merck, India), were used as received. Aqueous solutions were prepared using Milli-Q water obtained by a Millipore purification unit (Waters Millipore).

Preparation of crown ether modified cellulose acetate membrane: The polymeric film was prepared by dissolving desired quantity of cellulose acetate and 18-crown-6 ether as the ion carrier in acetone by constant stirring for 12 h using magnetic stirrer. A homogeneous colourless transparent slurry was obtained, which was spread on a clean, dried glass plate, showing good miscibility with no phase separation. After the solvent evaporation, the resulting membrane was peeled off from the glass plate by immersing in distilled water. The resulting membrane had a thickness of 72.2 µm.

Characterization of membrane

Scanning electron microscopy (SEM): SEM micrograph of the membrane was studied using scanning electron microscope apparatus (JEOL Model JSM- 6390LV).

Water content study: Water content of the membrane (surface area of 3 cm^2) was obtained after soaking membrane in distilled water at different time intervals and the membrane was weighed followed by mopping it with filter paper and weighed. The wet membrane was placed in an oven at appropriate temperature and the dry weight of the membrane was determined [16]. The water content was calculated by using eqn.1 :

$$Q_w^m = \frac{\text{Wet weight of membrane} - \text{Dry weight of membrane}}{\text{Dry weight of membrane}} \quad (1)$$

Water sorption of the aqueous electrolytic (NaCl, KCl) solution through the membrane was estimated by the water uptake. The rate constant (k) of the water content is expressed as:

$$-kt = \ln\left(\frac{Qw_{max} - Qw}{Qw_{max}}\right) \quad (2)$$

where Qw_{max} is the maximum water content. Mole uptake by membrane having certain area per unit time called water flux (f) of the membrane (mol s^{-1} cm^{-2}) can be estimated using the following equation:

$$f = \frac{W_{wet} - W_{dry}}{m \times t \times a} \quad (3)$$

where W_{wet} is the weight of wet membrane, W_{dry} is the weight of dry membrane, m is the effective molecular weight of the solution (H_2O, NaCl, KCl), t is time interval and a is the effective area of membrane (cm^2). The water sorption on the membrane having per unit volume is called porosity (p) of the membrane can be expressed as:

$$p = \frac{Q_w \cdot W_{dry}}{\rho \times a \times l} \quad (4)$$

where ρ is density of the solutions (H_2O, KCl and NaCl) and *l* is the thickness of dry membrane.

Conductance-time study: The membrane surface area of 1 cm^2 was fixed in glass cell and equilibrated with 1 M NaCl and KCl solutions separately. Solutions were changed with fresh solutions before each measurement. Conductance-time experiments were carried out in a conductance measuring cell is illustrated in Fig. 1, using 25 mL of 0.01-0.20 M NaCl/KCl, while the receiving phase was 150 mL of 0.001 M NaCl/ KCl. The conductance of the equilibrated membrane and the change in the ionic solute concentration in receiving phase was measured by digital conductivity meter (Autoranging Conductivity/TDS Meter, TCM 15+, India) having1.03 cm^{-1} as cell constant. Solutions of receiving phase were stirred by glass rod to increase the reproducibility of the conductivity sensor.

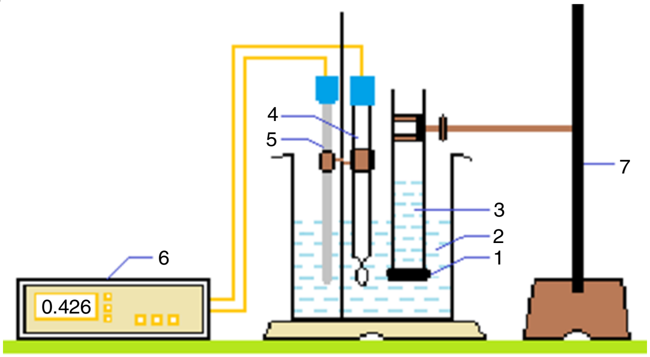

Fig. 1. Schematic representation of conductivity cell used in conductance time study experiments: membrane (1), receiving phase (2), source phase (3), conductivity sensor (4), automatic temperature compensation (5), conductivity meter (6) and stand (7)

Aqueous solution of different compositions of KCl and NaCl were used for ion transport through it under concentration gradient. Membrane/solution conductance time measurements data were noted and the important electrochemical parameters such as permeability (P), flow (F) and flux (J) for the system under study which vary with concentration, were also derived.

The permeability (P) of the ions through membrane was calculated using eqn. 5:

$$P = \frac{F}{A} \tag{5}$$

where F is the membrane flow (cm s^{-1}) and A is the effective membrane area. Flow (F) of material through the membrane was expressed as follows:

$$F = \frac{V}{t} \ln \frac{C_t}{C_i} \tag{6}$$

where V is volume of the aqueous electrolyte solution in glass cell, t is the time of transport (s), C_i is the initial conductance in the receiving phase and C_t the conductance in receiving phase at appropriate time. Membrane flux (J) denotes permeation rate with concentration difference.

The membrane flux can be defined by the following expression:

$$J = P.\Delta c \tag{7}$$

RESULTS AND DISCUSSION

The SEM micrographs of the polymeric membrane at different magnifications (500x and 1500x) are shown in Fig. 2a-b. Both SEM micrographs exhibited a very smooth and dense surface, which show a predominant effect of crown ether in the membrane morphology. The non-porous character of polymeric film signifies the homogeneous character of the membrane. The homogeneity of membrane was also developed due to presence of specific pore size of the crown ether moiety.

The water content of composite polymeric membrane decreases with time as shown in Fig. 3a-c. The hydrophilicity of the membrane was determined by performing a water uptake as a function of time. The hydrophilicity of the membrane was low due to the presence of lone pair-lone pair repulsion in the intracavity of crown ether, thus declined the the solvation of solutions (H_2O, NaCl, KCl) and resulted in the deterioration of the membrane hydrophilicity.

The values of rate constant (k), water flux (f) and porosity (p) in water are given in Table-1. In case of water uptake and water sorption of (NaCl, KCl) solution, it was observed that the water uptake rate is higher in first hour and then it decreases slightly (Table-1, Fig. 4a and 4d). Initially, water enters to the membrane film by engaging the pore in the membrane then diffuse at very low diffusion rate through the membrane film. When all pores engaged with water then only diffusion process occurs, resulting in the decrease water uptake rate.

It was also observed that by increasing the electrolyte solution concentration, the values of water flux decreased (Fig.

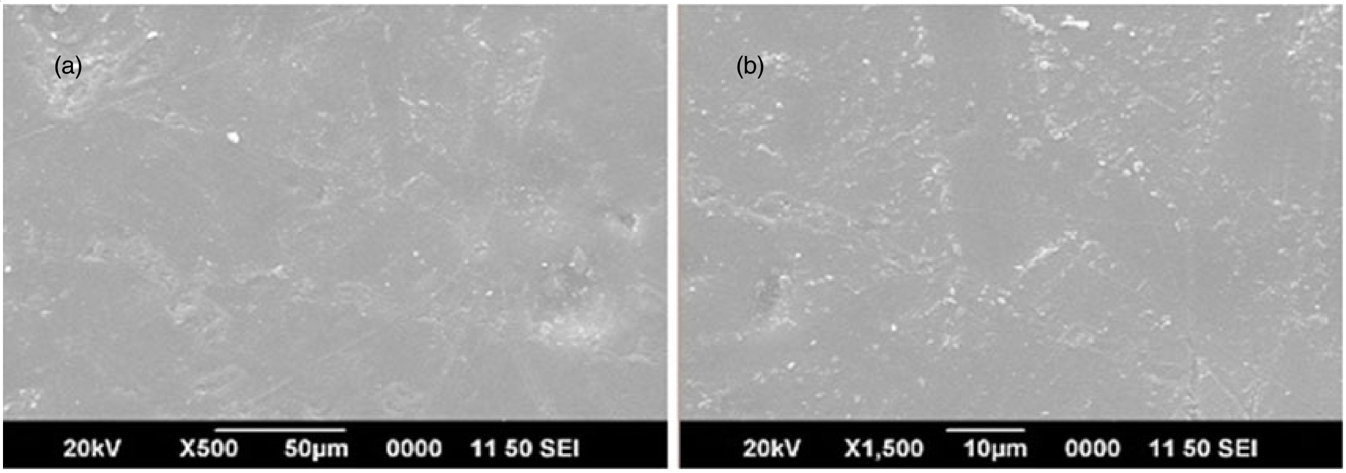

Fig. 2. SEM micrograph of 18-crown-6 modified cellulose acetate membrane with magnification (a) 500x and (b) 1500x

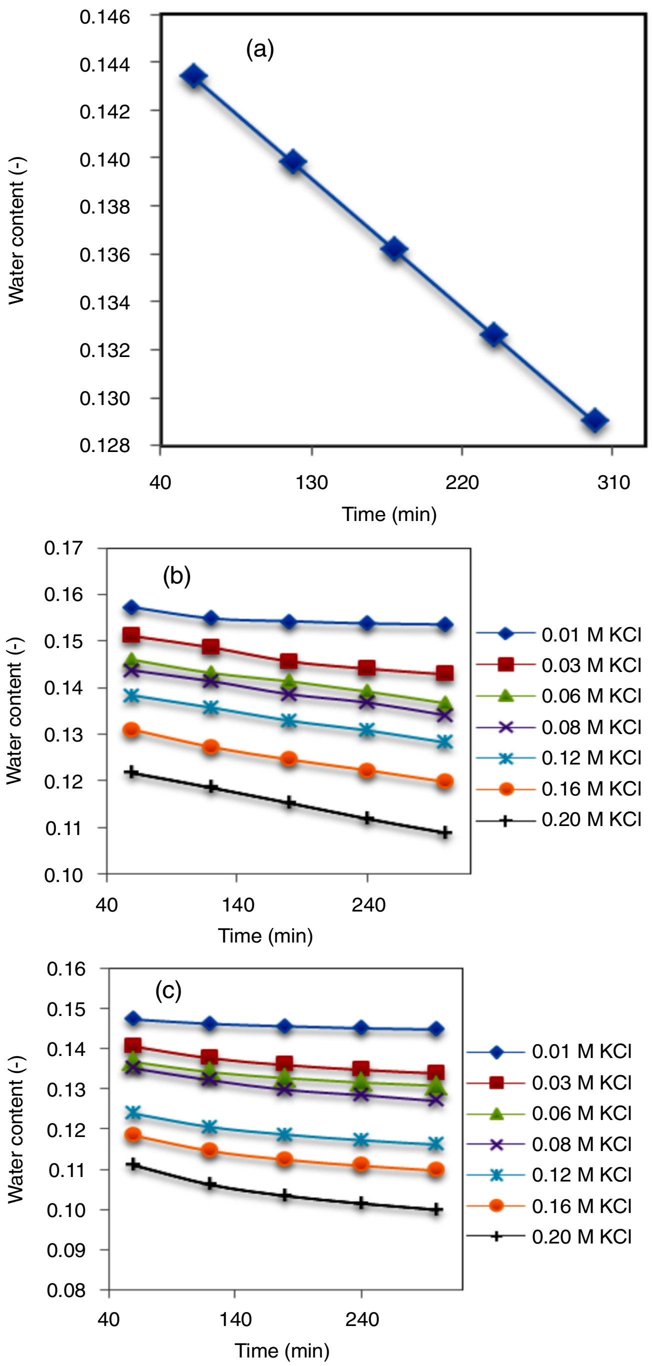

Fig. 3. Performance of water content with time using distilled water (a) aqueous KCl solution (b) and aqueous NaCl solution (c)

TABLE-1
TIME DEPENDENT DATA OF RATE CONSTANT (k), WATER FLUX (f) AND POROSITY (p) IN DISTILLED WATER

Time (min)	Rate × 10^3 (s^{-1})	Water flux × 10^8 (mol cm^{-2} s^{-1})	Porosity
60	1.191	1.526	0.1369
120	0.463	0.746	0.1339
180	0.284	0.491	0.1323
240	0.198	0.364	0.1308
300	0.149	0.288	0.1293

4b-e, i). The reason is attributed due to the osmosis phenomenon. Simultaneously, the porosity of the membrane also decreases with increasing time and increasing the electrolyte concentration; due to incorporation of crown ether in the membrane matrix as illustrated in Fig. 4c-f.

Conductance of the receiving phase increases with increasing time due to the transport of permeate through membrane as shown in Fig. 5. In case of NaCl solution, the permeability, flow and flux increased with the increase concentration of the receiving phase but it decreases with increasing time as shown in Fig. 6b, d and f. Then the passage of ions through the cellulose acetate crown ether membrane decreases with time (Table-2). In aqueous KCl solution, permeability, flow and flux values increases with increasing concentration (Table-2) and also increasing time as shown in Fig. 6a, c and e. The average value of membrane phase ion transport (Na^+ and K^+), effective fixed charge density and solute rejection are given in Table-3.

TABLE-3
IMPORTANT MEMBRANE PARAMETERS
DATA OF THE MEMBRANE

S. No.	Important membrane parameters
1	Average Na(I) ion transport in membrane phase = <0.8141>
2	Average K(I) ion transport in membrane phase = <0.8791>
3	Average effective fixed charge density, $<\phi X^m>=<0.2204M>$ for NaCl/Membrane system.
4	Average effective fixed charge density, $<\phi X^m>=<0.2434M>$ for KCl/Membrane system.
5	% Solute rejection, R_s^{max} (NaCl) = 14.69%
6	% Solute rejection, R_s^{max} (KCl) = 18.21%

Due to presence of fixed charges, ionic adsorption occurs onto the membrane interface which can be expressed by Gibbs equation [17] as membrane adsorption capacity (meq/g):

$$q = \frac{\Delta C.V}{m} \qquad (8)$$

TABLE-2
CONCENTRATION DEPENDENT DATA OF PERMEABILITY (P), FLOW (F) AND FLUX (J) IN NaCl AND KCl ELECTROLYTE SOLUTIONS

Concentration (M)	NaCl electrolyte solution			KCl electrolyte solution		
	Permeability × 10^{-5} (cm s^{-1})	Flow × 10^{-5} (cm^3 s^{-1})	Flux × 10^{-5} (mol cm^{-2} s^{-1})	Permeability × 10^{-5} (cm s^{-1})	Flow × 10^{-5} (cm^3 s^{-1})	Flux × 10^{-5} (mol cm^{-2} s^{-1})
0.01	2.563	8.050	0.023	1.918	6.022	0.017
0.03	2.283	7.170	0.067	2.062	6.475	0.060
0.06	2.957	9.282	0.175	2.297	7.212	0.135
0.08	3.178	9.981	0.252	2.467	7.745	0.195
0.12	3.430	10.77	0.408	2.840	8.918	0.338
0.16	3.513	11.03	0.558	3.263	10.25	0.518
0.20	4.387	13.78	0.873	3.740	11.74	0.743

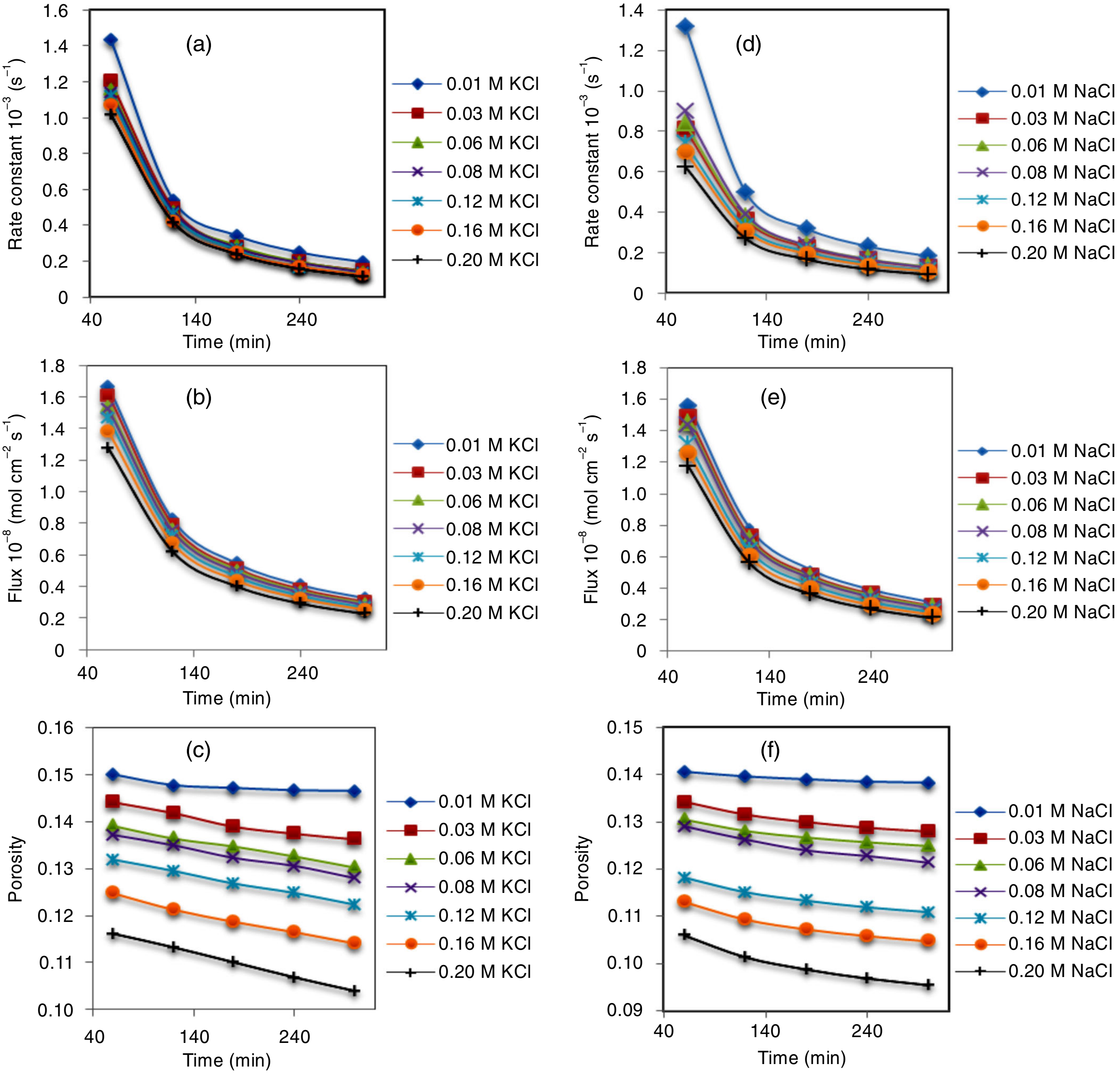

Fig. 4. The rate, flux and porosity performance using KCl (a-c) and NaCl (d-f) solutions

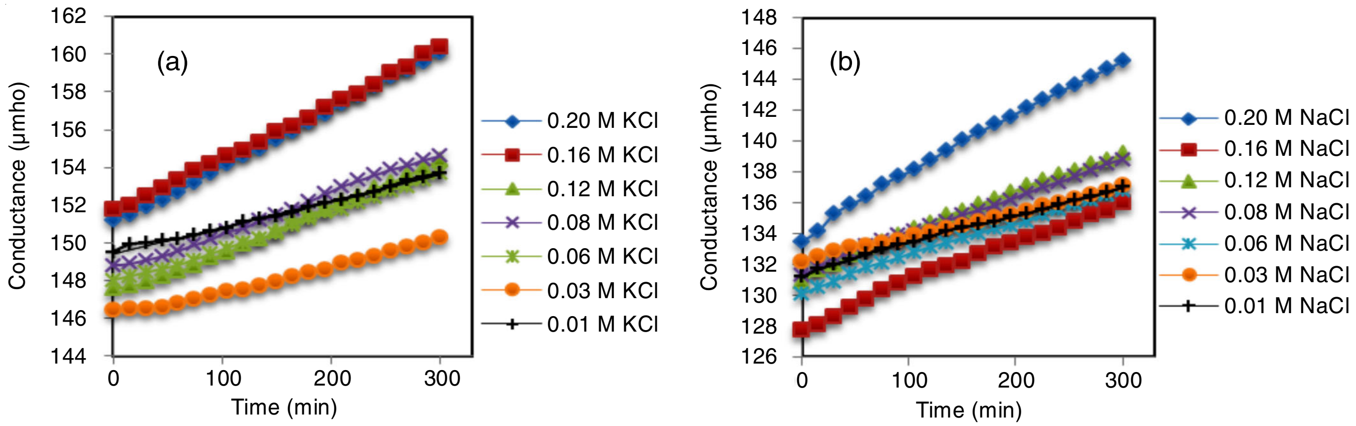

Fig. 5. Effect of conductance with time of the prepared membrane using KCl (a) and NaCl (b) solutions

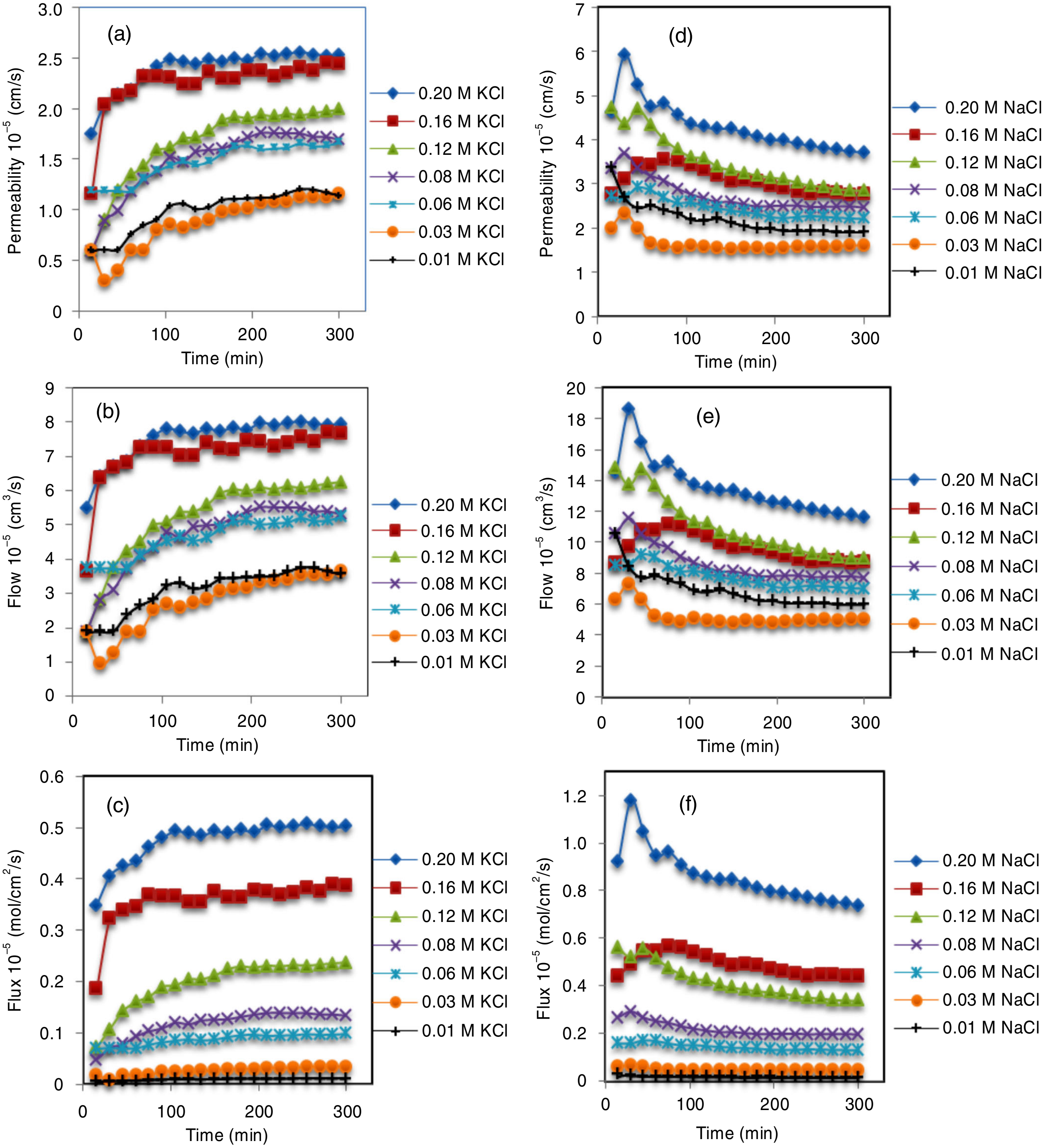

Fig. 6. Effect of permeability, flux and flow rate on the prepared membrane using KCl (a-c) and NaCl (d-f) solutions

where $\Delta C = (C_{ext} - C_{eq})$; C_{ext} and C_{eq} denotes the external and equilibrium concentrations of electrolyte, respectively; V is volume of electrolyte solution and m is the mass of the dried membrane. The adsorption capacity of membrane with electrolyte concentration is illustrated in Fig. 7.

Membrane hydrodynamic resistance (R_m) depends on the compactness of the membrane and pore dimension. As electrolyte concentration varies, the membrane compactness alters its performance. The dependence of membrane hydrodynamic resistance with electrolyte concentration is shown in Fig. 8.

The hydrodynamic resistance (R_m) is proportional to the electrolyte concentration with exponent (h), *i.e.* $R_m \alpha C_e^h$ where, h denotes membrane compaction coefficient and possesses the value of 0.09 (NaCl) and 0.065 (KCl), respectively, which indicates that the concentration range of NaCl or KCl does

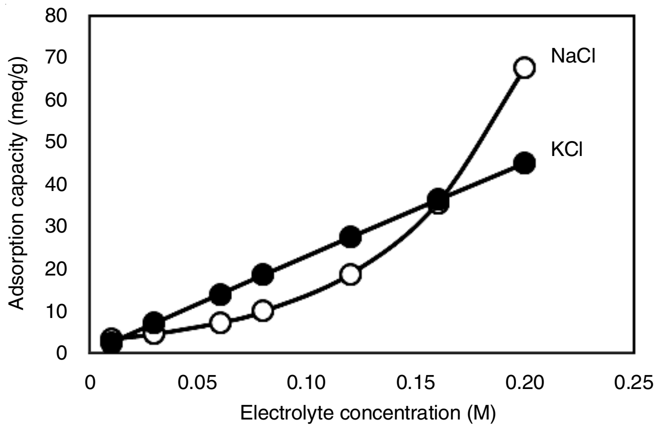

Fig. 7. Membrane adsorption isotherm in NaCl and KCl aqueous solutions of varying concentrations

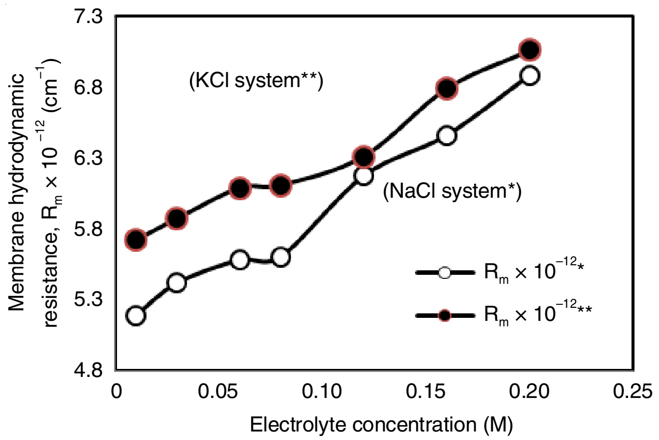

Fig. 8. Dependence of membrane hydrodynamic resistance on the electrolyte concentration

not deteriorate the membrane performance. However, the prepared membrane was more stable in KCl environment.

Conclusion

In this work, a hydrophobic 18-crown-6 modified cellulose acetate membrane was prepared with improved the antifouling property. The water sorption of aqueous KCl solution was greater than aqueous NaCl solution, due to selectivity of K^+ ions. The co-mixed membrane showed a change in flux and permeability values with different concentrations of KCl and NaCl solutions. The value of fluxes and permeability increases in K^+ ions than Na^+ ions, which indicates the K^+ selectivity of the prepared membrane. The SEM micrograph shows the homogeneity of the membrane. The outcome of the study is to separate Na^+ from K^+ using crown ether modified cellulose membrane. The studied membrane was capable to separate the Na^+ and K^+ ions electrochemically since both ions possess similar characteristics in a mixture.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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