



Research Article

Ion Transport through Surfactant Modified Cellulose Acetate Phthalate Membrane in Acidic Medium

A.K. Tiwari* and Z.F. Khan

Department of Chemistry, DDU Gorakhpur University, Gorakhpur -273009 (U.P.), India

*Corresponding author's email: dr_aktiwari@rediffmail.com

Abstract

Cellulose acetate phthalate (CAP) membrane was interacted separately with aqueous HCl solution and aqueous HCl with sodium dodecyl hydrogen sulphate (SDS) as a surfactant and their characteristic properties were determined on the basis of water content, conductance-time and membrane potential data. The possibility of electrochemical modification of cellulose acetate phthalate membrane upon immobilization of the anionic surfactant (SDS) has been also explored. Variable concentration of HCl solutions were used across a cellulose acetate phthalate membrane for membrane potential. The data has been used to interpret the variation of permselectivity, effective fixed charge density and Donnan distribution ratio of membrane.

Keywords: Water content; Membrane potential; Permselectivity; Effective fixed charge density; Ion transport number and Donnan distribution ratio.

Introduction

New technological developments necessary for producing greater quantities of water and protecting the quality of waters have begun to appear, particularly since the 1960s. Several new unit processes for water and waste water treatment have been developed. These include the membrane processes as a group, which can be divided into pressure driven (reverse osmosis and ultrafiltration and electrically driven (electro dialysis and transport-depletion) process (Spiegler and Laird, 1980). The membrane separation processes are thought to be especially useful in water renovation because they allow separation of dissolved material from one another or from solvent, with no phase change. Cellulose acetate phthalate is one of the potential hydrophilic organic polymers that can be used to improve hydrophilicity of membrane. Cellulose acetate phthalate shows the best performance membrane due to its high productivity and separation performance as well as it has good membrane characteristics in terms of high hydrophilicity properties, pore properties and membrane morphological structure (Rahimpour and Madaeni, 2007). Cellulose acetate phthalate has a superior characteristics compare to cellulose due to the presence of numerous acidic and carbonyl functional groups on its

structure. Greater affinity of Cellulose acetate phthalate to water, leads to longer time for the solvent exchange between the water and the polymer. Cellulose acetate phthalate may play a role as an antifouling agent. Cellulose acetate phthalate, belonging to cellulose esters, is prime among derived natural polymers and is sensitive to biodegradation. Cellulose esters are used to prepare miscible blends with polyester and other polymer. Cellulose esters have the ability to form hydrogen bonds, because the esters have –OH and C=O groups hence, the polyblends of polymer and CAP can create good material for numerous applications required in day to day life. The study of the properties of these blends creates an interest in the research world (Bhat and Jois, 2014). SDS is an effective surfactant. Surfactants have an inherent tendency to accumulate at interfaces depending upon the nature of the interface and that of the surfactants (Rosen, 1989; Fridrikhsberg 1986). Accordingly, properties which depend on the interfacial character of a system exhibit alteration in the presence of such surfactant. SDS is the sodium salt of dodecyl hydrogen sulphate class of organics. It consists of a 12-carbon tail attached to a sulfate group, its hydrocarbon tail combined with a polar head group give amphiphilic properties that allow it to form micelles (Singh and Tiwari, 1987). Alteration in the ion selective character of the membrane on

immobilization of SDS has been examined with the objective of exploring the possibility of obtaining cation selective membrane endowed with the enhanced permselectivity. Membrane systems allow transmission of ions and molecule with varying degrees of restriction and membrane behavior may undergo modification as a result of accumulation of surfactant in the interfacial region (Lakshminarayanaiah, 1976; Zook, 1996; Singh *et al.*, 1998). One of the processes of separation is membrane potential phenomena. Membrane potential studies are traditionally used for the characterization of membranes.

Experimental

Chemicals and Membrane Materials

Cellulose acetate phthalate (LR Grade, CDH, India)-were used for membrane formation. Hydrogen Chloride (AR Grade, S.D .Fine Chemicals, India) and Tetra Hydro Furan (AR Grade, SDFCL ,India) were used as received and SDS (AR Grade, CDH ,India).

Membrane Preparation

Cellulose acetate phthalate (CAP) membrane have been prepared via solvent vaporization method. A simple method was used for the formation of the (CAP) membrane. To ensure uniformity of composition, a casting solution prepared by dissolving 4g CAP and 4g of polyvinyl chloride in 36ml of tetra hydro furan by constant stirring for 1-2 days on magnetic stirrer. It was spread on a clean dried glass plate with the help of a scale. The glass plate was kept in an electric oven at 60degree for about half an hour to remove the solvent. The plate was then immersed in distilled water to detach the membrane. The membrane was kept pressed between a folded filter paper to avoid wrinkles. There after the membrane was kept pressed between the folders of a filter paper. Its dimensional characterization is done by using suitable technique in dry and wet state. The prepared membranes were cut in three pieces of equal size.

The membranes were dried in incubator at 60 degree regularly to get constant dry weight. Thickness of these membranes are measured with the help of screw gauge having least count, 1×10^{-3} cm. The water content of the membrane in water and in different concentrations of HCl solution for 24 hrs at room temperature were carried out. The improvement of selectivity of the membrane is noticed by using adsorption of surfactant on the surface of the membrane. The modification of the membrane surface material concerns with the hydrophilic/hydrophobic balance properties and its relationship with the hydration state.

Kinetic Studies of H^+ Ion Exchange from the Membrane to Surrounding Aqueous Solution

Kinetics of specific ion exchange of Cellulose acetate phthalate membrane was observed in HCl solution of varying concentrations. Its ion exchange kinetics was time dependent phenomenon. H^+ ion exchange with the solution

of different concentration of HCl solution is determined by the pH meter.

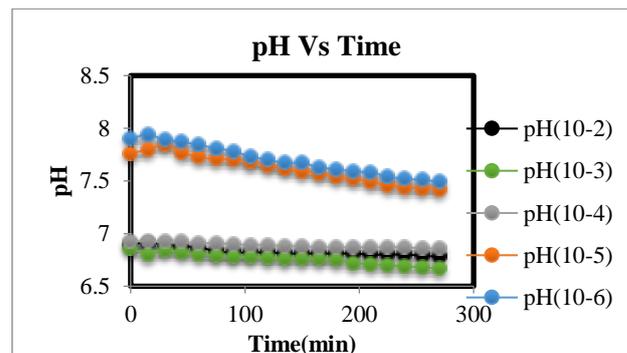


Fig. 1: Time dependence of H^+ exchange with external aqueous solution of HCl.

Membrane Water Content

The membrane was conditioned by immersing it 24h in water at 25°C after which it was removed from the water, blotted with a filter paper to remove any excess water; the weighed weight was recorded as wet weight. The membrane was then dried for 24hrs in desiccator and weighed; its weight was recorded as dry weight. The water content was calculated as:

$$Q_w^m = (\text{wet weight} - \text{dry weight}) / \text{dry weight} \quad (1)$$

Membrane Water Content with Different Concentration of Aqueous HCL Solution

Cellulose acetate phthalate membrane of size dipped in aqueous solution of HCl of different concentration for 24 hrs. Water content was determined.

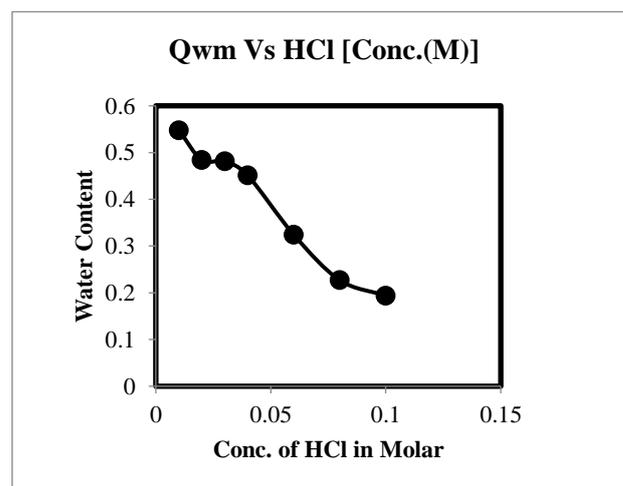


Fig. 2: Dependence of membrane water content on the concentration of the aq. HCl solution.

Membrane Water Content in Aq. HCl Solution along with Surfactant

Cellulose acetate phthalate membrane of size $2 \times 2 \text{ cm}^2$ was dipped in different concentration of aqueous solution of HCl mixed with surfactant SDS. The membrane was immersed in each one of the solutions for 24 hours. Water

content, was determined and concerned dependence is shown in Fig.3.

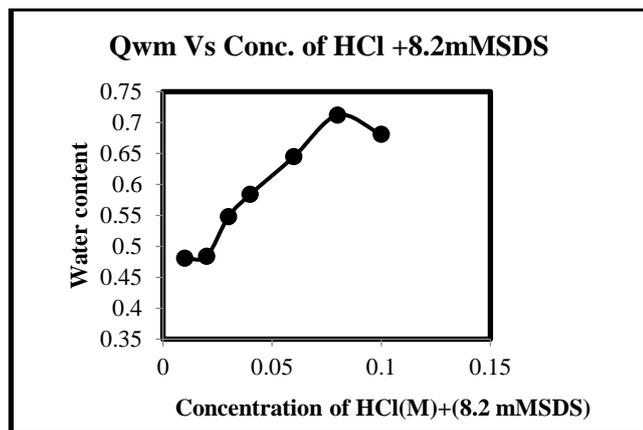


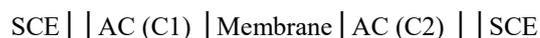
Fig 3: Dependence of water content on the concentration of aq. HCl solution along with SDS of concentration=8.2mM (CMC of SDS)

Membrane Conductance and Potential Measurements

The membrane was then kept in hydrogen chloride solution of the desired concentration for about 24 hours to allow equilibration. The solution was renewed before starting conductance measurements. For Conductance measurement, the measurement of electrical conductivity was carried out using digital conductivity meter (Auto-ranging Conductivity meter TCM15⁺).

For Membrane Potential measurements the experimental set-up used is reported elsewhere (Singh *et al.*, 1985). The potential/conductance- time measuring cell was made of glass (Tiwari *et al.*, 2015). A piece of the membrane under investigation was fixed in glass-cell. Desired solution of known concentration of electrolyte was kept on either side of the supporting substrate to allow equilibration. The potential across the membrane structure was measured with the help of a digital multimeter using calomel electrodes. The solutions were connected to saturated calomel electrode through salt bridge. The solutions were renewed after allowing equilibration and potential measurements were carried out repeatedly until a constant potential difference across the membrane could be measured.

The electrochemical set up used for membrane potential measurements may be represented as



An electrical potential difference existing across a membrane separating two electrolyte solution is called membrane potential. This potential difference arises as a consequence of electro neutrality requirement initially an extremely small net charge transfer may occur, but this charge transfer results in an electrical potential difference and enforces their compensation (Lakshminarayanaiah, 1966; Harris, 1960). The permeability of ion species migrating across a membrane depends upon the properties of the ion and the membrane. If the membrane has no fixed

charges, the membrane potential is equivalent to diffusion potential (Teorell 1935; Meyer and Sievers, 1936).

Results and Discussion

Kinetics of specific ion exchange capacity of CAP membrane was observed in HCl solution of varying concentrations. Its kinetics of ion exchange was Concentration dependent phenomenon. H⁺ ion uptake from the solution of different concentration of HCl solution is determined by the pH meter. If the dissociation of carboxylic group in cellulose acetate phthalate is affected, pH changes upon equilibration with HCl at different pH values were recorded. The data given in graph show that increases the HCl concentration the carboxylic group in cellulose acetate phthalate releases the H⁺ in solution and pH value decreases when the H⁺ ion of hydronium ion of solution reacts or attracted with OH group of Cellulose acetate phthalate membrane to become unstable. Then membrane give to hydronium ion in solution and membrane becomes negatively charged. This clearly indicates progressive suppression of the dissociation of cellulose acetate phthalate with aqueous solution of HCl membrane is protonated and charge effectiveness factor increases as H⁺ concentration increases.

When the cellulose acetate phthalate membrane are interacted in HCl solution, H⁺ ion interacted with hydroxyl group, due to interaction of H⁺ ion on hydroxyl group, -OH₂ generated at free -OH group. These -OH₂ removed as water molecule in solution, which increase the H⁺ concentration in the solution. Thus, hydrogen ion concentration increases in the solution therefore pH value decreases with time. Negative charge generated on the membrane. This indicates that membrane bearing negative charge and membrane becomes cation selective.

The membranes exhibit considerable water content. CAP of size 2x2cm² was immersed in aqueous solution of HCl of varying concentrations for 24hrs. Water content, was determined for every concentration. Water content of the membrane in aq. solution of HCl is less than in along with presence of surfactant SDS. Cellulose acetate phthalate of size 2x2cm² was immersed in aqueous solutions of Cellulose acetate phthalate membrane give good water content. Its percentage is 50%. Water content also increases when cellulose acetate phthalate membrane mixed with sodium lauryl sulphate its percentage is 70%.

Conductance is typically measured in aqueous solutions of electrolytes. Electrolytes are substance containing ions that mean solution of ionic salts or of compounds that ionize in solution (Nagarale *et al.*, 2004). The ions formed in solution are responsible for carrying the electric current. Electrical conductance is measured for different concentration of HCl with anionic surfactant (SDS) and without SDS different concentration of HCl was used to measure conductance. To observe the effect of surfactant on cellulose acetate

phthalate membrane readily increases rather than without surfactant of HCl concentration. The graph is shown below:

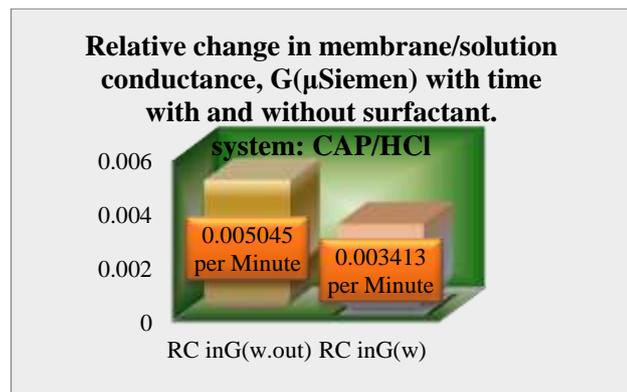


Fig. 4: Variation of conductance of membrane systems against time, without and with SDS.

Membrane potential measurements have been carried out using variable concentration of HCl in the presence of cellulose acetate phthalate membrane. The counter-ion transport number across the membranes was estimated by membrane potential measurement in HCl solution (0.01M mean concentration to 0.10 concentration) using the TMS theory.

The membrane potential is a consequence of the ability of a membrane to allow passage of ions of an electrolyte (Singh *et al.*, 1987; Singh *et al.*, 1985; Higuchi *et al.*, 1987). For the description of membrane potential across cellulose acetate phthalate membrane the Teorell-Meyers-Siever theory is used (Lakshmi Narayanaiah ., 1976) according to which the membrane potential is given by the equation-

$$(\Delta\phi)_{I=0} = \frac{RT}{F} (t_-^m - t_+^m) \ln C_1/C_2 \quad (2)$$

Where, t_+ and t_- denote transport numbers of ions in the membrane phase, R is gas constant, F is Faraday number and T is the temperature in degrees Kelvin (Glasstone and Lewis 1966). The membrane potential data for cellulose acetate phthalate membrane shows that the membrane potential decreases with increase in concentration.

The maximum value of membrane potential (Zhou *et al.*, 1998) is given by the equation

$$[(\Delta\phi)_{I=0}]_{\max} = \frac{RT}{F} \ln \frac{c_1}{c_2} \quad (3)$$

Values of $[(\Delta\phi)_{I=0}]_{\max}$ calculated using Eq.(2) show that the maximum value of membrane potential decreases with increase in concentration of HCl solution. This obviously arises because of progressive enhancement of the negative charge borne by the membrane.

The values of apparent transport number of hydrogen ion in the membrane phase was calculated using the equation

$$t_-^m = \frac{[(\Delta\phi)_{I=0}]}{2[(\Delta\phi)_{I=0}]_{\max}} + 0.5 \quad (4)$$

Estimated value of t_+^m decreases with increase in acid concentration. The reason of the reduction of cation transport number is the breakdown of the Donnan exclusion. The electrical character of a membrane is usually expressed in terms of fixed charge density. Effective fixed charge density of a membrane can be expressed in terms of permselectivity defined as

$$P_s = \frac{(t_-^m - t_+)}{(1 - t_-)} \quad (5)$$

Where, t_- denotes the transport number of the anion in solution phase. t_-^m denotes the transport number of the anion in membrane phase. Permselectivity is related to effective fixed charge density, $\phi\bar{X}$, by Eq. (5)

$$\phi\bar{X} = 2 \frac{C_e P_s}{\sqrt{1 - P_s^2}} \quad (6)$$

Permselectivity and fixed charge density values derived using Eqs (4) and (5) respectively are shown in Figs.7 and 8.

It is clear from the Fig.5 that effective fixed charge densities change with concentration. Fixed charge groups influenced the membrane permselectivity. Permselectivity increases with mean concentration. Effective fixed charge density increase with mean concentration due to shrinkage in the membrane texture.

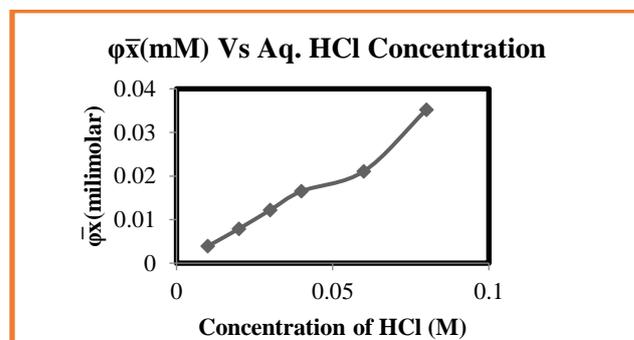


Fig. 5: Change in fixed charge density with concentration of aqueous HCl solution.

The Donnan distribution ratio, ζ_{Donnan} varies with solution of pH as shown in Fig. 6.

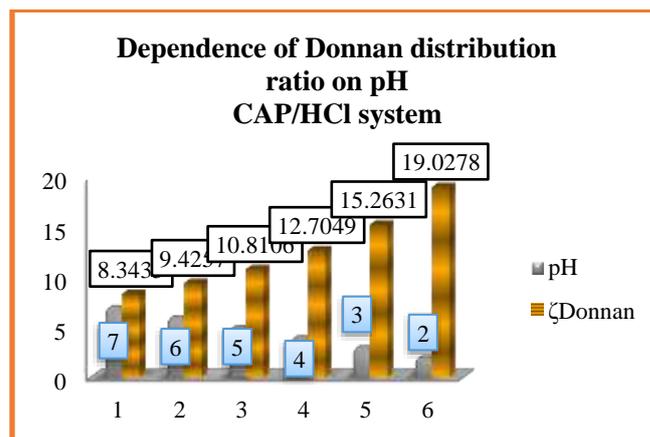


Fig. 6: Dependence of Donnan distribution ratios on pH

The Donnan distribution ratio is the result of a balance between the electrostatic forces and the osmotic forces affecting the permeating ions which varies with the pH of the surrounding aqueous solution. Membrane performance can be expressed in terms of solute rejection, S_R as:

$$S_R(\text{without}) = A + B [C_{\text{mean}}(M)] \quad (7)$$

Where, A and B are constants for the system and these are related through an inequality as $(0 < A < B < 1)$. In presence of SDS, at its cmc value; solute rejection, S_R , can be expressed as:

$$S_R(\text{with}) = P + Q [C_{\text{mean}}(M)] \quad (8)$$

Where, P and Q are constants for the surfactant modified membrane system. P and Q follow the inequality as $(Q < 0 < P < 1)$. Constants of these systems can be correlated as: $(1 > P > A < B > Q < 0)$

The effect of the surfactant, SDS on the CAP/HCl membrane system is different. As HCl concentration increases, solute rejection performance decreases and it is expected that at approximately 1M HCl, rejection performance will tend to zero. Membrane system, without surfactant, is expected to enhance the rejection performance with the increase of the HCl concentration. It is obvious that surfactant SDS, changes the behavior of CAP membrane. Water content variation patterns of the both membranes are different with the concentration variation of the external solution of HCl. This difference may be due to the difference in heterogeneity.

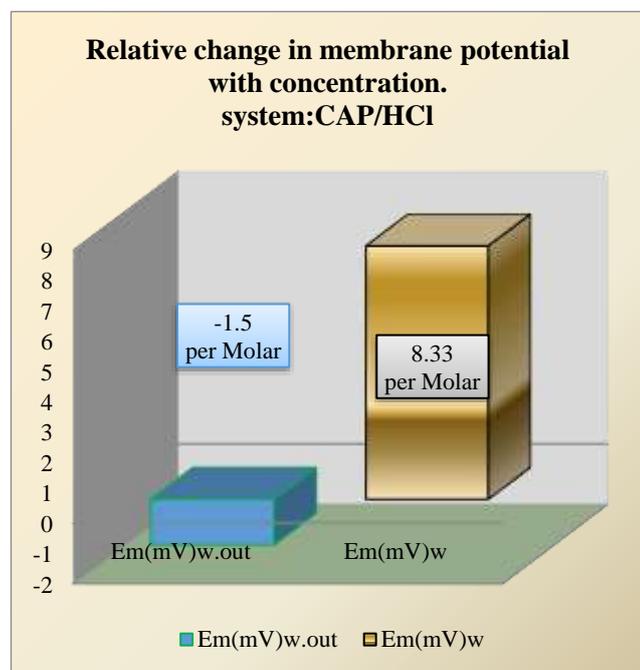


Fig. 7: Relative change in membrane potential with change in mean concentration of external HCl solution

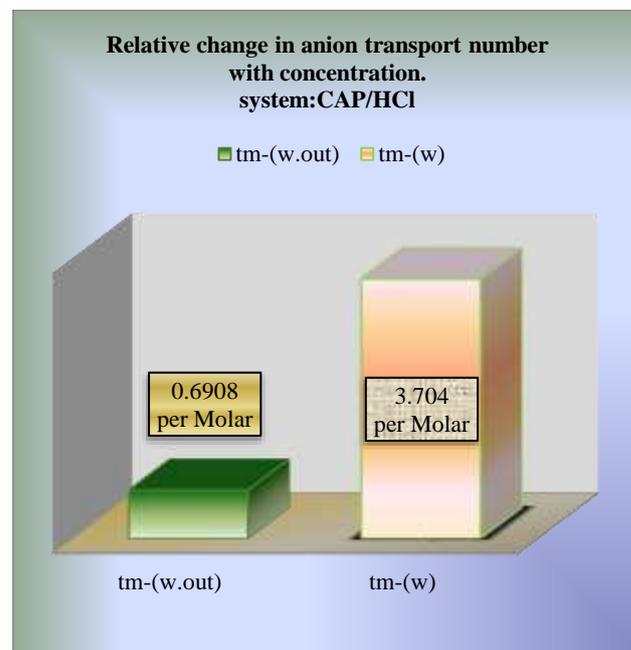


Fig. 8: Relative change in anion transport number with change in mean concentration of external HCl solution

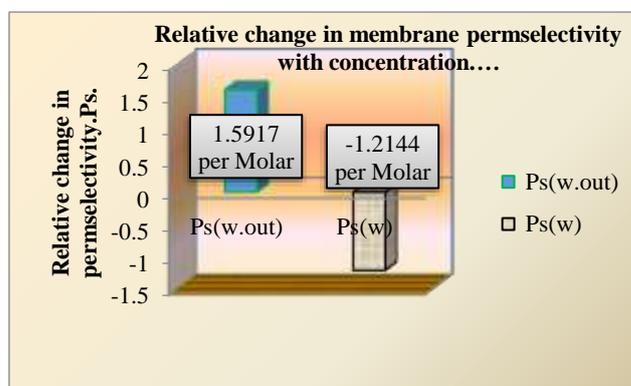


Fig. 9: Relative change in membrane permselectivity with change in mean concentration of external HCl solution.

As bar diagrams show, SDS affects to considerable extent CAP membrane behaviors which are shown in terms of electrochemical parameters like membrane potential, transport number, permselectivity and effective fixed charge density. All these parameters vary with acid and surfactant concentrations.

Conclusion

1. Both membranes show water content in their texture, but water content variation pattern is different.
2. Heterogeneity in both membranes varies with external HCl concentration.
3. In CAP membrane system, permselectivity increases with the increase of external HCl concentration but in CAP/SDS system permselectivity variation pattern is opposite. These observations are due to the Donnan

exclusion. In CAP, the Donnan exclusion is maintained by the system and in presence of SDS; there is break down of the Donnan exclusion.

4. Effective fixed charge density of the both membrane systems increases with External HCl concentration.
5. The counter-ion and co-ion transport number differ each other to the considerable extent in the membrane phase.
6. With increase of hydrogen ion concentration in the surrounding solution, Donnan distribution ratio increases steadily.
7. Along with counter-ion and co-ion transport, water molecules also possess passage through the membrane under HCl concentration difference.
8. Since there exists heterogeneity in the membrane, there must be a symmetry factor for the both membranes.
9. In presence of SDS, it is possible to expect the acidic environment may be reduced due to ion exchange between SDS and HCl.

Acknowledgements

The authors thank the Head, Department of Chemistry, DDU Gorakhpur University, Gorakhpur for providing laboratory facilities and the University Grant Commission, New Delhi for financial support. Authors gratefully acknowledge Prof. Kehar Singh for helpful discussions.

References

- Ali A, Yunus RM, Awang M, Johari A and Mat R (2014) Effect of cellulose Acetate phthalate (CAP) on characteristics and Morphology of Polysulfone/ Cellulose Acetate phthalate Blend Membrane. *Applied Mechanics and Materials* **493**: 640-644. DOI: [10.4028/www.scientific.net/AMM.493.640](https://doi.org/10.4028/www.scientific.net/AMM.493.640)
- Bhat DK and Jois HSS (2014) Miscibility and cellulose acetate phthalate blends. *Procedia material science* **5**: 995-1004 DOI: [10.1016/j.mspro.2014.07.388](https://doi.org/10.1016/j.mspro.2014.07.388)
- Conway BE (1952) *Electrochemical Data*, Elsevier Pub. Co, Amsterdam Houston
- Fridrikhsberg DA (1986) *A Course in Colloid Chemistry*. Mir Moscow.
- Glasstones S and Lewis D (1966) *Elements of Physical Chemistry*. 2nd Edition McMillan and Co Ltd London.
- Higuchi A and Nakagawa T (1990) Surface modified polysulfone hollow fibers. III. Fibers having a hydroxide group. *Journal of Applied Polymer Science* **41**(9-10): 1973-1979. DOI: [10.1002/app.1990.070410904](https://doi.org/10.1002/app.1990.070410904)
- Kobatki Y and Kamo N (1973) Transport process in charged membrane. *Prog Polymer Sci Jpn* **5**: 257
- Lakshminarayanaiah N (1976) *Membrane Electrodes*. Academic Press New York.
- Rahimpour A and Madaeni SS (2007) Polyether sulfone (PES)/CAP blend ultrafiltration membrane: Preparation morphology performance and antifouling properties. *Journal of Membrane Science* **305**: 299-312. DOI: [10.1016/j.memsci.2007.08.030](https://doi.org/10.1016/j.memsci.2007.08.030)
- Rosen MJ (1989) *Surfactants and Interfacial Phenomena* Wiley New York
- Singh K Shabd R and Srivastava V N (1981) Ion exchange membrane potential: Polyethylene and styrene- divinyl benzene copolymer based cation exchange membrane. A novel electrochemical method for simultaneously measuring diffusing coefficient and ion transference number. *Indian Journal Chemistry* **20**(4): 391.
- Singh K Tiwari AK (1987) Membrane potential studies on cholesterol liquid membrane. *Journal of Membrane Sci.* **34**: 155-163. DOI: [10.1016/S0376-7388\(00\)80029-0](https://doi.org/10.1016/S0376-7388(00)80029-0)
- Singh K Tiwari AK and Rai JP (1985) Studies on Electroactivity of Anion Exchange Alumina Membrane Supported on a polyvinylidene Fluoride Matrix. *Indian J Chem* **24A**: 825-827
- Spiegler KSL and Kedem ADK (1980) *Principles of desalination*. Academic Press New York.
- Tiwari A.K, Sonkar R and Tiwari PK (2015) Electrochemical Characterization of Cellulose Acetate Butyrate-Prmutit Composite Membrane in Aqueous Uni-Uni Valent Electrolyte Solutions. *Int J Appl Sci Biotechnol.* **3**(2): 337-341. DOI: [10.3126/ijasbt.v3i2.12748](https://doi.org/10.3126/ijasbt.v3i2.12748)
- Zhou H, Shi Z and Dong S (1998) A novel electrochemical method for simultaneously measuring diffusion coefficient and ion transference number. *Journal of Electroanalytical Chemistry* **443**(1): 1-3. DOI: [10.1016/s0022-0728\(97\)00446-4](https://doi.org/10.1016/s0022-0728(97)00446-4)
- Zook LA (1996) Mass transport enhancements in supermagnetic microbed/ion exchange polymer composites. *Electrochem Soc Interface* **5**: 51