

Effects of electrolytes on ion transport in Chitosan membranes

N. N. Rupiasih

Department of Physics, Faculty of Mathematics and Natural Sciences, Udayana University, Kampus Bukit Jimbaran, Badung, Bali 80362, Indonesia
Group Research Material Sciences and Technology-Polymer and Biomaterial

E-mail: rupiasih@unud.ac.id

Abstract. Recently, charged polymer membranes are widely used for water purification applications involving control of water and ion transport, such as reverse osmosis and electrodialysis. In this study, we have explored the effects of electrolyte solutions on ion transport properties of chitosan synthetic membranes via concentration gradient driven transport. Also, the water uptake of those membranes, before (control) as well used membranes have studied. The membrane used was chitosan membrane 2%. The electrolyte solutions used were HCl, KCl, CaCl₂, MgCl₂ and AlCl₃, with various concentrations of 0.1 mM, 1 mM, 10 mM, 100 mM and 1000 mM. Ion transport experiments were carried out in a cell membrane model which composed of two compartments and the potential difference of membrane was measured using Ag/AgCl calomel electrodes. Those measurements were conducted at ambient temperature 28.8 °C. The results showed that the current density (J) increased with increased in concentration gradient of solution. The current density was higher in electrolyte solution which has higher molar conductivity than those of a solution with a small molar conductivity. Meanwhile the current density was smaller in electrolyte solution which has larger Stokes radii than those of a solution with small Stokes radii. Except membrane which has been used in HCl solution, the water uptakes of the used membranes were greater than the control membrane. These results can develop and validate a common framework to interpret data of concentration gradient driven transport in chitosan synthetic membranes and to use it to design of membranes with improved performance.

1. Introduction

Chitosan is a biopolymer composed of glucosamine and N-acetyl glucosamine units linked by 1-4 glucosidic bonds, has found wide application in the biomedical field, such as controlled drug release, biomaterial and tissue engineering [1, 2]. The development of synthetic membranes had been inspired by the fact that the selective transport through biological membranes which known as *ion exchange*

³Author to whom any correspondence should be addresses: rupiasih@gmail.com

membranes (IEM) [2]. Ion exchange membranes discriminate cation and anions, thus they should have a high transport number for counter-ions. Such membranes have the potential applications as a new functional material in separation of ionic materials, mostly used in the solutions containing multi components, such as electrodialytic concentration of seawater to produce sodium chloride, demineralization of sugarcane juice, demineralization of saline water, etc [3].

Most ion exchange membranes have made of synthetic polymers; only a few were from natural polymers e.g. chitosan, cellulose and alginate [2, 4]. Chitosan can be used as an *anion exchange membranes (AEM)* directly, cellulose derivatives such as cellulose phosphate, cellulose acetate and alginate were used as *cation exchange membranes (CEM)* [2].

Since the use of ion exchange membranes has become more diverse, requirements for membranes with unusual properties have increased. These requirements have led to the development of various kinds of newly functionalized ion exchange membranes. Recently the ion exchange membranes has been used not only for the traditional applications, such as electrodialysis concentration or desalting of solutions, diffusion dialysis to recover acids and electrolysis of sodium chloride solution, but also in various fields as a polymeric film having ionic groups [5].

The water uptake in membranes is considered to be a key factor in the ion and water transfer and in polarization processes in electromembrane systems [6]. Also, the water transport mechanism into the polymer is particularly important for assessing the suitability of these materials as drug delivery systems and membranes in separation processes [7]. Concentration polarization is a well-known phenomenon occurring at the interface between an ion exchange membrane and an electrolyte solution when the current passes through it or if there is concentration gradient of electrolyte solution [6].

The objective of this study was to investigate the effects of electrolyte solutions on the ion transport properties of chitosan synthetic membranes. The transport processes were conducted through concentration gradient driven transport and all transport experiments were obtained under the same conditions. Moreover, the water uptake experiments were carried out to investigate the effect of those electrolyte solutions to hydrophilic properties of the membrane.

2. Materials and methods

2.1 Transport in chitosan membranes

HCl, KCl, CaCl₂, MgCl₂, AlCl₃ and other reagents used in this study were obtained from commercial sources. The membrane used was chitosan membrane 2%. The electrolyte solutions used were HCl, KCl, CaCl₂, MgCl₂ and AlCl₃, with various concentrations of 0.1 mM, 1 mM, 10 mM, 100 mM and 1000 mM. Ion transport experiments were carried out in a cell membrane model which composed of two compartments (1 and 2) and the potential difference of membrane was measured using Ag/AgCl calomel electrodes. Those measurements were conducted at ambient temperature 28.8 °C.

2.2 Water uptake

The membrane was cut into fixed size 1 cm × 1 cm. They were soaked in distilled water for 0.5 – 24 h, then taken out, wiped and then weighed. These samples were then dried in a vacuum oven overnight and the dry weight measured. The water uptake was determined by the following equation [1, 8].

$$\text{Water uptake (\%)} = \frac{w_w - w_d}{w_d} \times 100$$

Where w_w is the weight of the wet membrane (g) and w_d is the weight of the dry membrane (g).

Table 1. Values of molar conductivity and Stokes radii for selected cations in this study.

Cations	Stokes radii ^a (nm)	Molar conductivity ^a (10 ⁴ S.m ² .mol ⁻¹)
H ⁺	0.026	349.8
Al ³⁺	0.125	189
Ca ²⁺	0.308	119
Mg ²⁺	0.346	106.1
K ⁺	0.437	73.55

^a From Ref. [9].

3. Results and discussion

3.1 Characteristic of potential difference (V) vs Log (C1/C2)

Figure 1 shows the potential difference (V) of membranes as function of Log (C1/C2) where C1 and C2 is concentration of solution in compartment 1 and compartment 2, when the membranes in contact with electrolyte solutions such as HCl, KCl, CaCl₂, MgCl₂ and AlCl₃. In general, Fig. 1 shows that the potential difference increased as increasing the logarithmic of C1/C2. This result is in accordance to the Nernst equation [10], which illustrates that the potential difference is due to differences in concentration in both compartments e.g. proportional to Log (C₁/C₂). The figure also show that except HCl solution, the increment of potential difference is more in electrolyte with greater Stokes radii than those of an electrolyte with a small Stokes radii and the graph look sharper.

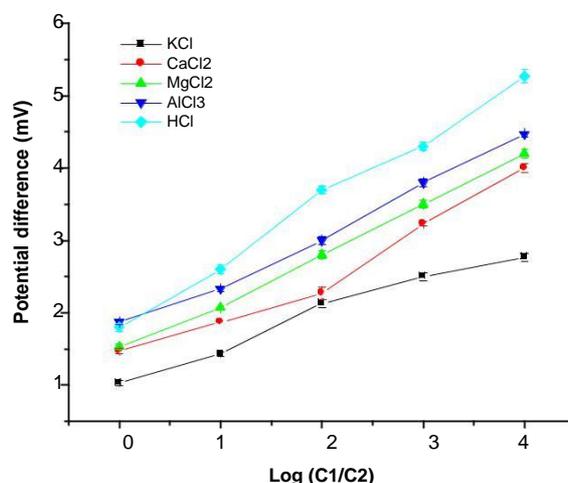


Figure 1. The potential difference (V) as a function of Log (C1/C2) for different electrolyte solutions. HCl, KCl, CaCl₂, MgCl₂ and AlCl₃.

3.2 Characteristic of current density vs. concentration gradient ($\Delta C/\Delta x$)

Figure 2 shows the current density (J) of membranes as function of gradient concentration ($\Delta C/\Delta x$). It shows that the current density is increased as increase in concentration gradient of electrolyte solution. This result is in accordance to Fick law, which states that the current density is proportional to concentration gradient of the electrolyte solution [10]. All curves show that at small concentration gradient ($\Delta C/\Delta x$) e.g. 0 mM/cm, 0.09 mM/cm and 0.99 mM/cm, the current density increased gently and at greater concentration gradient e.g. 9.99 mM/cm the increase was sharp and at the highest

concentration gradient 99.99 mM/cm, the increased is very sharp. The same result has been reported at our previous publication [2].

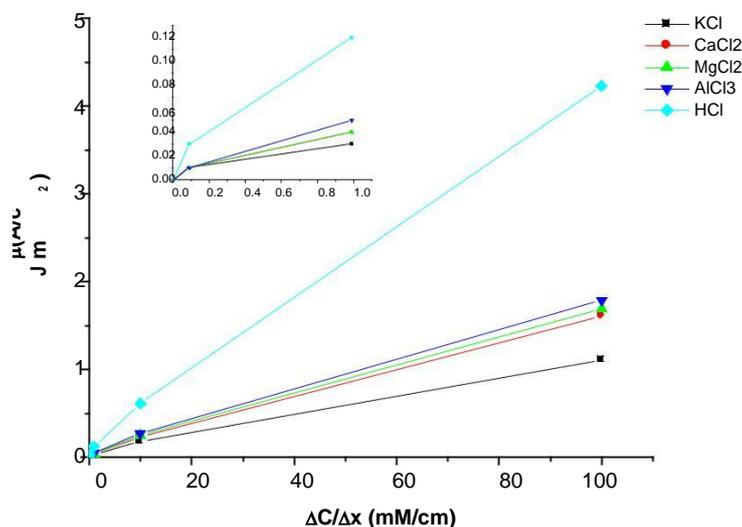


Figure 2. The current density (J) as a function of concentration gradient ($\Delta C/\Delta x$) for different electrolyte solutions: HCl, KCl, CaCl₂, MgCl₂ and AlCl₃.

3.3 Effect of electrolyte solutions on current density

The relation between current density and electrolyte solutions (HCl, KCl, CaCl₂, MgCl₂ and AlCl₃) in various concentrations gradient 0, 0.09 mM/cm, 0.99 mM/cm, 9.99 mM/cm and 99.99 mM/cm show in Fig. 3a and 3b. Figure 3a, the graphs draw in ascending order of molar conductivity of the electrolyte solutions and Fig. 3b, the graphs draw in ascending order of Stokes radii of the electrolyte solutions. The both figures are shown just to describe them easily. The graphs showed that the current density (J) increased with increased in concentration gradient ($\Delta C/\Delta x$) of solution. The same result has been reported at our previous publication [2]. The current density is higher in electrolyte solution which has higher molar conductivity than those of a solution with a small molar conductivity (Fig. 3a). This means that the efficiency of ion transport in the membrane is better in the electrolyte solution which has higher molar conductivity. Meanwhile the current density is smaller in electrolyte solution which has larger Stokes radii than those of a solution with small Stokes radii (Fig. 3b). These results explain about the effect of electrolyte solutions to the characteristics of ion transport property of chitosan membrane which expressed as current density via concentrations gradient driven transport.

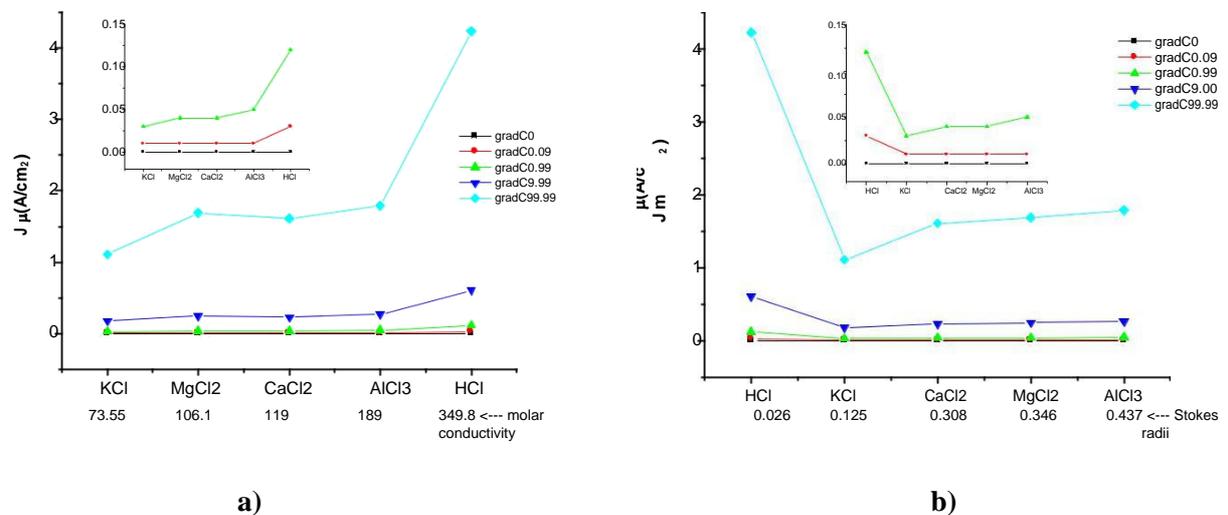


Figure 3. The relation between current density and electrolyte solutions (HCl, KCl, CaCl₂, MgCl₂ and AlCl₃) in various concentrations gradient 0, 0.09 mM/cm, 0.99 mM/cm, 9.99 mM/cm and 99.99 mM/cm. a) having different molar conductivity and b) having different Stokes radii.

3.4 Water Uptake

The water uptake (hydrophilicity) of the membranes, control and used membranes were investigated (Fig. 4a and 4b). Except membrane which has been used in HCl solution, the water uptakes of the used membranes were greater than the control membrane (Fig. 4b). Fig. 4a shows control membrane and the membranes which have been used in HCl, KCl and MgCl₂ solutions reached maximum of water uptake after 6 h, membranes which have been used in AlCl₃ solutions reached maximum of water uptake after 12 h and membranes which have been used in CaCl₂ reached maximum of water uptake very fast that is after 2 h. These means after exposed to those electrolyte solutions some changes have occurred in structure of the membranes which improve their hydrophilic property.

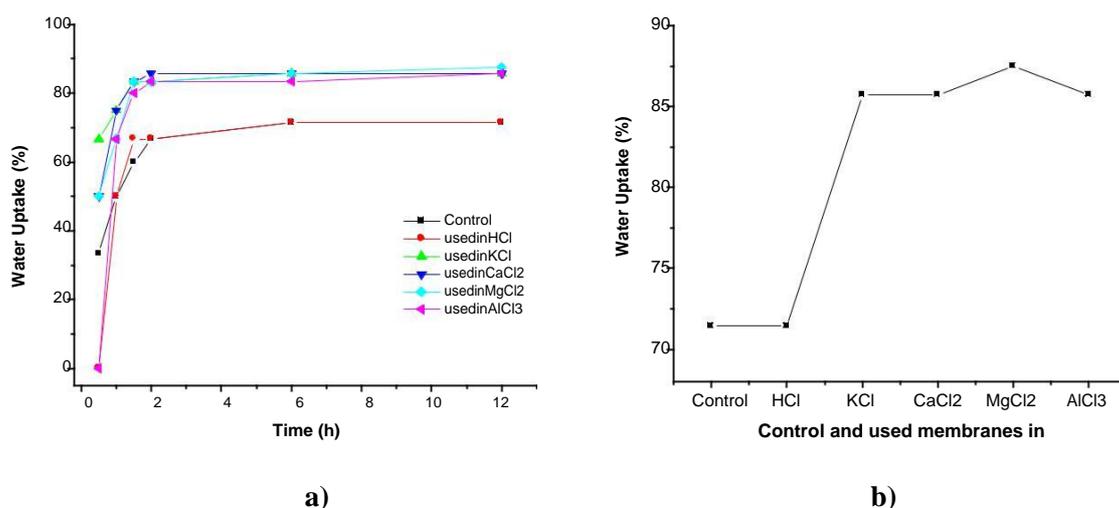


Figure 4. Water uptake of chitosan membrane, control and used membranes in various electrolyte solutions: HCl, KCl, CaCl₂, MgCl₂ and AlCl₃. a) Water uptake as function of times and b) The percentage maximum of water uptake (%) of chitosan membrane.

4. Conclusion

The study about the effects of electrolyte solutions on ion transport properties of chitosan membranes via concentration gradient driven transport has been described. It was observed that the current density (J) increased with increased in concentration gradient of solution. The current density is higher in electrolyte solution which has higher molar conductivity than those of a solution with a small molar conductivity. Meanwhile the current density is smaller in electrolyte solution which has larger Stokes radii than those of a solution with small Stokes radii. Except membrane which has been used in HCl solution, the water uptakes of the used membranes were greater than the control membrane. These revealed that electrolyte solutions affected the hydrophilic property of the membranes. Those results described that how electrolyte solutions affected ion transport properties of chitosan synthetic membranes via concentration gradient driven transport.

5. Acknowledgments

This work was partially supported by the Ministry of Research, Technology and Higher Education, Republic of Indonesia, under Fundamental Research Grant of Udayana University, Year Budget 2015/2016 are highly acknowledged. Also thanks to my student 'Made Rasmini' for helping in data collection.

6. References

- [1] Ricardo MP da Silva, Sofia G-C, Julio S-R'n, Joa~o F-M and Rui L-R, 2008 *Biomacromolecules* 9, 2132–2138.
- [2] Rupiasih NN, Puspita YE and Sumadiyasa M 2015 *Journal of Physics: Conference Series* 622, 012004.
- [3] Nagarale RK, Gohil GS and Vinod K-S 2006 *Advances in Colloid and Interface Science* 119, 97 – 130.
- [4] Xin C, Jiahao L, Zhicheng F and Zhengzhong S 2005 *Journal of Applied Polymer Science* 96, 1267-1274.
- [5] Sata T, 1991 *Reviews of Applied Electrochemistry* 26, *Journal of Applied Electrochemistry* 21, 283-294.
- [6] Aguilera VM, Mafe S, Manzanares JA and Pellicer J 1991 *Journal of Membrane Science* 61, 177-190.
- [7] Magdalena G-D, Jadwiga O-C 2012 *Progress on Chemistry and Application of Chitin and Its ...*17, 59-66.
- [8] Rebecca SLY, Kaisong Z and Bradley PL 2013 *Membranes* 3, 182-195.
- [9] Choi J-H, Lee H-J and Moon S-H 2001 *Journal of Colloid and Interface Science* 238, 188–195.
- [10] Hobbie, Russel K. 1978, *Intermediate Physic for Medicine and Biology*. Second Edition. John Willey and Son. Singapore, 45-105.