

Transport phenomena in chitosan synthetic membranes with emphasis on the effect of variations in the ratio of matrix/solvent

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Abstract. The object of this research was investigating the transport phenomena of chitosan synthetic membranes with emphasis on the effect of variations in the ratio of matrix/solvent. The study was focused on the effect of amount of chitosan as matrix and electrolytes solutions on the characteristics of current density of chitosan membranes. A series of chitosan membranes with various ratios of components was used such as 1%, 2%, 3% and 4%. The electrolytes solutions, NaCl and CaCl₂, with various concentrations, 0.1 mM, 1 mM, 10 mM, 100 mM and 1000 mM, were used. Ion transport processes were carried out in a cell membrane model which composed of two compartments named compartment 1 and 2, and the potential difference was measured using a pair of Activon AEP jnt Single 12 x 120 mm calomel electrodes. All the measurements were conducted at room temperature, 28.8 °C. The result showed that the current density increased with some parameters e.g. increased in the ratio of concentration of solution, C1:C2; increased in the amount of chitosan, 1%, 2%, 3% and 4%; and increased in the size of Stokes radii of the selected cations, Na⁺ and Ca⁺².

Keywords: Chitosan synthetic membrane, electrolyte solution, current density, ion diffusion

1. Introduction

Chitosan is a biopolymer composed of glucosamine and N-acetyl glucosamine units linked by 1-4 glucosidic bonds. It is a cationic polysaccharide obtained by de-N-acetylation of chitin under alkaline conditions [1-3]. Recently, chitosan has attracted great interest due to its specific properties such as biodegradability, biocompatibility, non-toxic, antibacterial, physiological inert and bioactivity [4-5]. These biological characteristics provide chitosan a wide field of applications as a material part in bio-environments systems, such as pharmaceutical and biomedical engineering, food industry, agriculture and wastewater treatment. Such applications involve as drug carriers, wound-healing agents, chelating

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agents, hemodialysis membranes and surgical dressing materials, biodegradable coating or film for food packaging, coating of seeds and leaves to improve plants' resistance to diseases, and coating of fertilizers and pesticides for their controlled release to soil [1, 5-10]. Chitosan is readily converted to fibers, membranes, coatings, powders and solutions, further enhancing its usefulness [1].

Chitosan membranes have been used for active transport of chloride ions in aqueous solution [1]. The other applications are as a carrier and/or a selective barrier controlling the transport rate of the substances involved, chitosan having a powerful chelating ability provides protection of the systems against destructive effects of heavy metal ions [11].

The development of synthetic membranes had always been inspired by the fact that the selective transport through biological membranes is enabled by highly specialized macromolecular and supramolecular assemblies based on and involved in molecular recognition [12], the use of membranes as ion exchanger. The ion exchange membrane has been used for the traditional applications, such as electrodialysis concentration or desalting of solutions, diffusion dialysis to recover acids, and electrolysis of sodium chloride solution. Recently it also used in various fields as a polymeric film having ionic groups [13] such as ion-exchange membranes for protein separation [14].

Most ion-exchange membranes are made of synthetic polymers; only a few are from natural polymers e.g. chitosan, cellulose and alginate [14]. Chitosan can be used as an anion-exchange membrane directly [15], cellulose derivatives such as cellulose phosphate [16], cellulose acetate [17] and alginate [18] are used as cation-exchange membranes.

In the present study, we prepared a series of chitosan membranes by varying the ratio of components e.g. matrix/solvent. The purpose of this work was to study of transport phenomena in those various synthetic membranes. The effects of concentration and electrolytes on their characteristics were also reported.

2. Materials and methods

2.1 Materials

NaCl, CaCl₂ and other reagents used in this study were obtained from commercial sources.

2.2 Transport in chitosan membranes

A series of chitosan membranes e.g. M1, M2, M3 and M4, have prepared by varying the ratios of components (matrix/solvent) such as 1%, 2%, 3% and 4% respectively. The electrolytes solutions used were NaCl and CaCl₂ with various concentrations, 0.1 mM, 1 mM, 10 mM, 100 mM and 1000 mM. Ion transport processes carried out in a cell membrane model which composed of two compartments named compartment 1 and 2, and the potential difference was measured using a pair of Activon AEP jnct Single 12 x 120 mm calomel electrodes. C1 and C2 is concentration of solution in compartment 1 and compartment 2, respectively. In the transport processes, C1 are varies as 0.1 mM, 1 mM, 10 mM, 100 mM and 1000 mM whereas C2 is kept constant 0.1 mM. All the measurements were conducted at room temperature, 28.8 °C.

3. Results and discussion

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

Figure 1a and 1b show the potential difference of membranes as function of Log (C1/C2) when the membranes in contact with NaCl and CaCl₂ solution, respectively. In general, Figure 1a and 1b show that the potential difference (V) increased as increasing the ratio of concentration, C1:C2. This result is in accordance to the Nernst equation (Hobbie, Russell K, 1978) [19], which illustrates that the potential difference is due to differences in concentration in compartment 1 and 2 e.g. proportional to Log (C₁/C₂). Both figures also show that the increased of potential difference in CaCl₂ solution was bigger compared with NaCl solution, the graph look sharper.

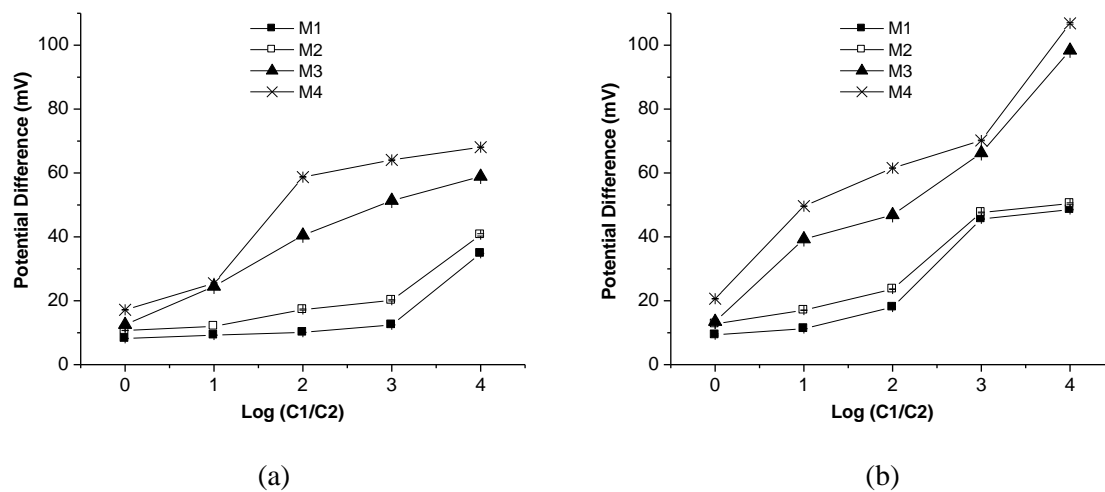


Figure 1. The potential difference (V) vs. $\text{Log}(C_1/C_2)$ graphs of chitosan membranes in contact with a) NaCl solution and b) CaCl₂ solution.

Figure 2a and 2b show the potential difference in each membrane in contact with various concentrations (0.1, 1, 10, 100 and 1000 mM) of NaCl and CaCl₂ solution, respectively. It shows an increased in the potential difference with increased in the amount of matrix constituents of membranes from 1%, 2%, 3% and 4% which named as membrane M1, M2, M3 and M4, respectively. This explains that increased in the amount of matrix constituent result a more positive membranes formed, which affects the diffusion characteristics of the membranes itself.

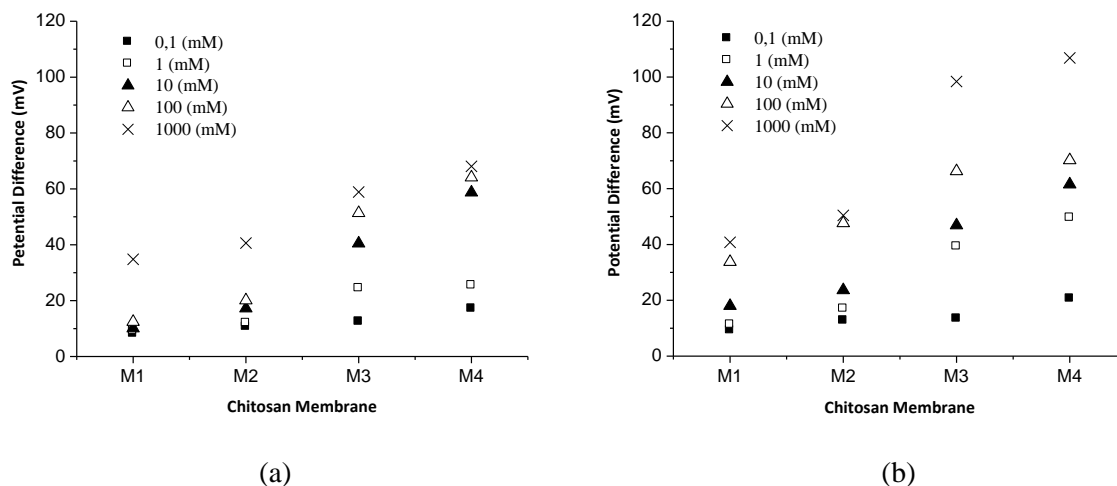


Figure 2. The potential difference (V) vs. chitosan membranes (M1, M2, M3 and M4) graphs in various concentrations e.g. 0.1, 1, 10, 100 and 1000 mM of a) NaCl solution and b) CaCl₂ solution.

3.2 Characteristic of current density vs. $\text{Log}(C_1)$

Figure 3 and Figure 4 show that at small ratios ($C_1 : C_2$ is small) e.g. 0.1 mM : 0.1 mM, 1 mM : 0.1 mM and 10 mM : 0.1 mM, the current density (J) increased gently. The increased is rising sharply at bigger ratios e.g. 100 mM : 0.1 mM and at the highest ratio e.g. 1000 mM : 0.1 mM, the increased is

very sharp. The both figures also show that the increased of the current density is greater when the membranes in contact with CaCl_2 solution compared with NaCl solution. This result can be described that the numbers of Cl^- ions in CaCl_2 solution are double compared in NaCl solution, that is one Cl^- ion for one Na^+ ion and two Cl^- ions for one Ca^{2+} ion. These mean that the driving force is double when the membranes in contact with CaCl_2 solution, the graphs in Figure 4 look sharper.

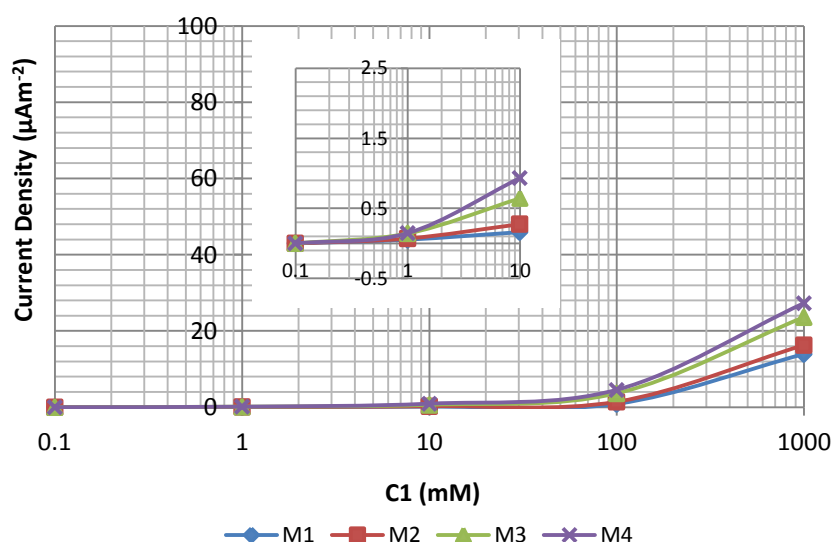


Figure 3. Current density vs. C_1 (concentration of NaCl solution in compartment 1) semi log graphs.

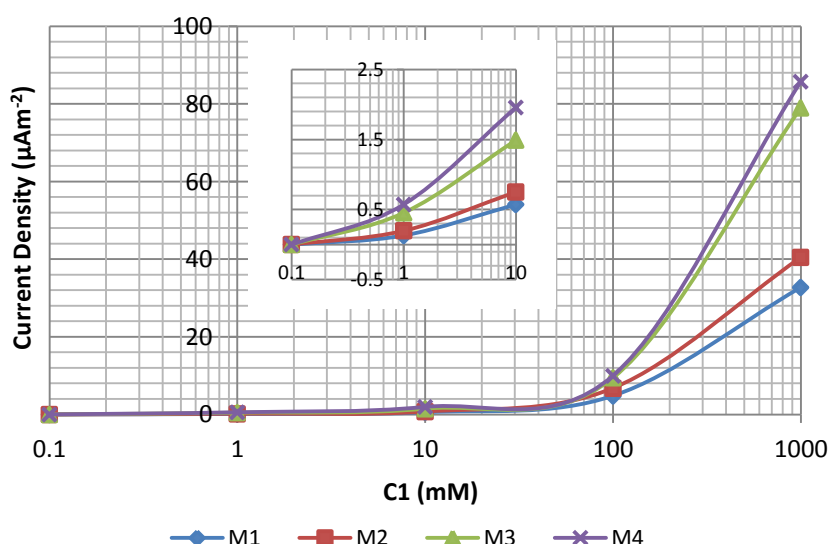


Figure 4. Current density vs. C_1 (concentration of CaCl_2 solution in compartment 1) semi log graphs.

Increasing the amount of matrix (chitosan) also affects ion transport characteristics of the membranes as shown in Figure 5. It shows that the current density is increased with increasing the amount of matrix e.g. 1%, 2%, 3% and 4% which named as membrane M1, M2, M3 and M4 respectively. This result is consistent with the increased in the value of the potential difference measured.

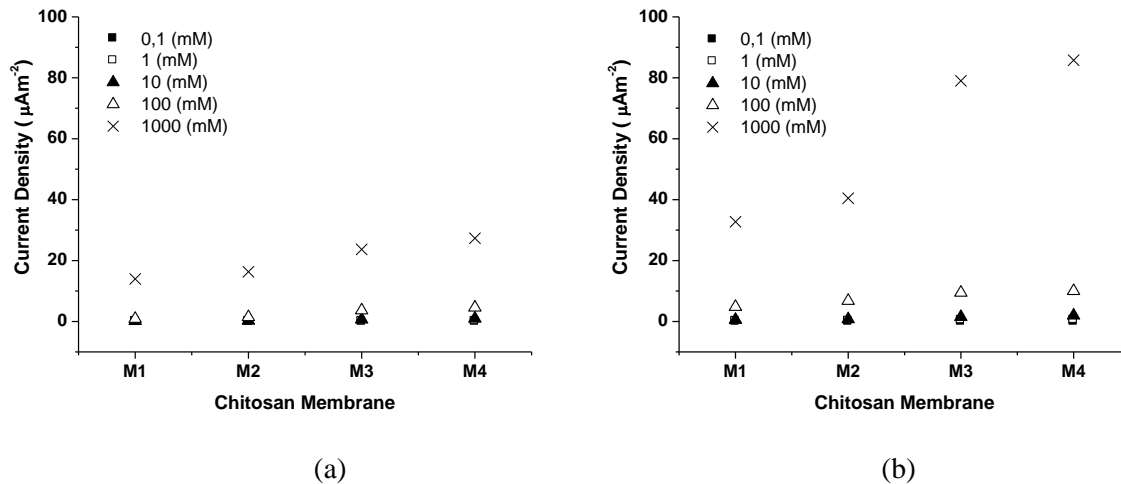
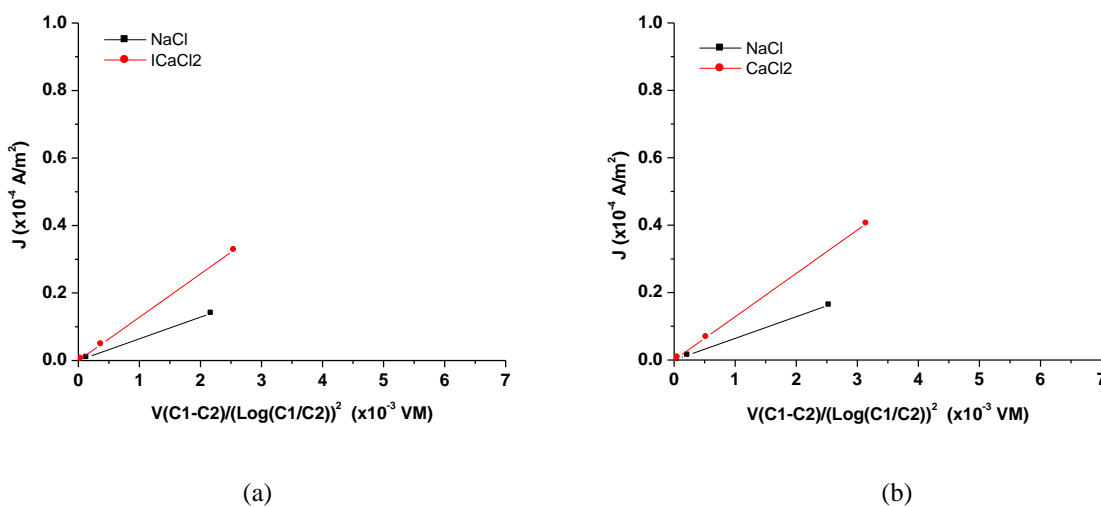


Figure 5. Current density vs. chitosan membranes (M1, M2, M3 and M4) graphs in various concentrations (0.1, 1, 10, 100 and 1000 mM) of a) NaCl solution and b) CaCl_2 solution.

3.3 Effect of electrolyte solutions on current density

Figure 6 describe the effect of electrolyte solutions to the ion transport characteristics of chitosan membranes. The graphs show similar pattern for all membranes, M1, M2, M3 and M4, e.g. the graph is sharper as membranes in contact with CaCl_2 solution compared with NaCl solution. This is in accordance with the increased in the size of Stokes radii of the selected cations, Na^+ and Ca^{+2} . The numbers of Cl^{-1} ions in CaCl_2 solution are double compared in NaCl solution, that is one Cl^{-1} ion for one Na^+ ion and two Cl^{-1} ions for one Ca^{+2} ion.



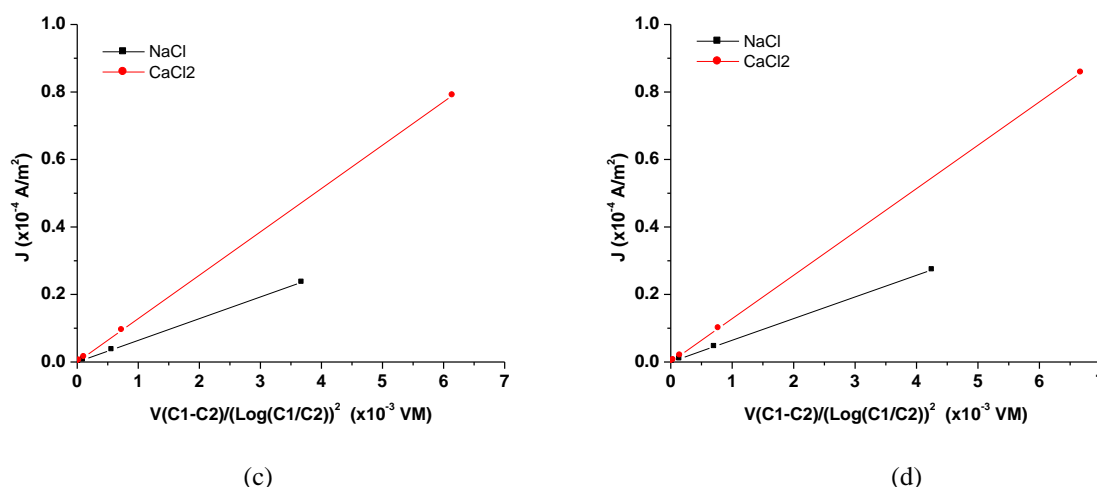


Figure 6. Current density vs. $\{V(C1-C2) / (\text{Log}(C1/C2))^2\}$, subsequently: a) M1, b) M2, c) M3 and d) M4.

4. Conclusion

The study about transport phenomena in chitosan synthetic membranes with emphasis on the effect of variations in the ratio of matrix/solvent has been described. The results showed that the current density is increased with some parameters such as increased in the ratio of concentration of solution, C1:C2; increased in the amount of matrix (chitosan), 1%, 2%, 3% and 4% which named as M1, M2, M3 and M4 respectively; and increased in the size of Stokes radii of the selected cations, Na⁺ and Ca⁺².

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