Desalination and Water Treatment
www.deswater.com

34 (2011) 257–265
October

1944-3994/1944-3986 © 2011 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2011.2892

Dominant impact of the α-L-guluronic acid chain on regulation of the mass transfer character of calcium alginate membranes

Keita Kashima, Masanao Imai*

Course in Bioresource Utilization Sciences, Graduate School of Bioresource Sciences, Nihon University, 1866 Kameino, Fujisawa, Kanagawa-pref. 252-0880 Japan
Tel./Fax: +81-466-84-3978; email: XLT05104@nifty.com

Received 3 September 2010; Accepted 3 January 2011

ABSTRACT

The dominant impact of the α-L-guluronic acid chain on regulation of the mass transfer character of calcium alginate membranes was investigated. The polymer frameworks of the membranes were successfully regulated by altering the mass fraction of homopolymeric blocks of α-L-guluronic acid (F_{GG}) in the entire molecular chain of alginate. Sodium alginate is well-known as a hydrophilic polysaccharide. Its molecular chain is composed of α-L-guluronic acid and β-D-mannuronic acid. The polymeric structure of calcium alginate is mainly constructed by intermolecular ionic bonds with homopolymeric blocks of the α-L-guluronic acid junction zone. The entire alginate polymer chain then forms into a swollen gel and a membrane. The water fraction of the swollen membrane and the mechanical strength changed with F_{GG}. The volumetric water fraction based on the swollen state of the membrane was evaluated from the gravitational water content (H_M). The change in the mass transfer mechanism of the membrane was evident in the effective diffusion coefficient, especially for the smaller molecules (e.g., urea). Good correlation between the volumetric water fraction and the effective diffusion coefficient strongly suggested that the mass transfer channels in the alginate membrane were dominantly regulated by the mass fraction of homopolymeric blocks of α-L-guluronic acid (F_{GG}). The relationship between the effective diffusion coefficient and the volumetric water fraction agreed with Yasuda's free volume theory. The tortuosity was markedly increased and the effective diffusion coefficient was reduced. In conclusion, the homopolymeric blocks of α-L-guluronic acid have a dominant impact on the mass transfer character in the calcium alginate membrane.

Keywords: Calcium alginate; β-D-mannuronic acid; α-L-guluronic acid; Membrane; Mass transfer; Effective diffusion coefficient

1. Introduction

Biopolymers produced from foods are expected to be employed as both food-enabling polymers and sustainable and environmentally friendly polymers. They have great potential as alternatives to various artificial polymers produced from petroleum. Alginic acid is abundantly produced by marine biological resources, especially brown seaweed. Alginates have been widely applied in the food industry as thickeners, suspending agents, emulsion stabilizers, gelling agents, and film-forming agents [1].

Sodium alginate is a well-known hydrophilic polysaccharide. The alginate molecular chain is constructed as a block co-polymer of β-D-mannuronic acid (Fig. 1a) and α-L-guluronic acid (Fig. 1b). Three types of blocks have been described previously: homopolymeric blocks of mannuronic acid (M-M), guluronic acid (G-G), and

*Corresponding author.

Presented at the AMS6/IMSTEC10, The 6th conference of the Aseanian Membrane Society in conjunction with the 7th International Membrane Science and Technology Conference, Sydney Australia, November 22–26, 2010

blocks with an alternating sequence in varying proportions (M-G) [2,3,4] (Fig. 1c).

The physical properties of sodium alginate strongly depend on environmental chemical factors (e.g., pH and total ionic strength). At near-neutral pH, the high negative charge of sodium alginates due to deprotonated carboxylic functional groups induces repulsive intermolecular and intramolecular electrostatic forces. A change in ionic strength in a sodium alginate aqueous solution significantly affects polymer chain extension [5,6].

Sodium alginate conveniently forms into a gel structure in the presence of divalent cations such as Ca^{2+}, resulting in a highly compacted gel network [6]. The variation in gel strength has been analyzed in terms of the modes of binding of cations by the various block structures that occur within the alginate molecule. Regions of homopolymeric blocks of α-L-guluronic acid chelate the metal ions because of the spatial arrangement of the ring and hydroxyl oxygen atoms and thus create a much stronger interaction [7]. These homopolymeric blocks of α-L-guluronic acid junction zones are mainly constructed of a cross-linked area called an "Egg-box," where the Ca^{2+} ions are located as the "Egg" components [8] (Fig. 1d). Alginate polymer networks are often employed and investigated as useful carriers for immobilized enzymes, drug-delivery capsules, [9] and food supplements [10,11,12]. In contrast, alginate membrane has not been so well investigated. It was previously supported by glass fiber [13] and has been found in hybrids with other polymer materials [14,15].

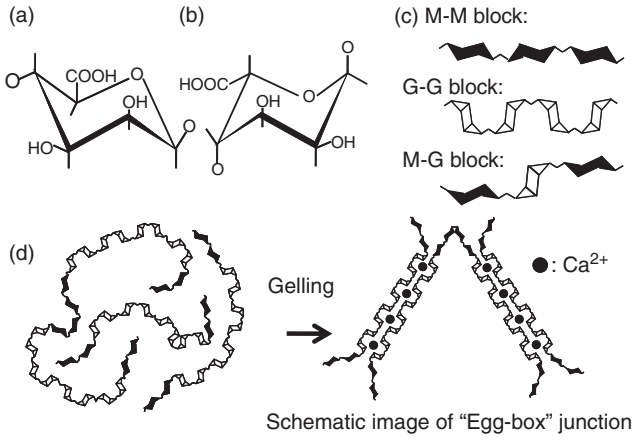

Fig. 1. Alginate composition. Alginate consists of two monomeric units: (a) β-D-mannuronic acid and (b) α-L-guluronic acid. (c) The three types of blocks have been previously described as homopolymeric blocks of mannuronic acid (M-M), guluronic acid (G-G), and blocks with an alternating sequence in varying proportions (M-G). (d) Structural formula of the calcium alginate molecular chain. Calcium alginate gel formation in the presence of calcium ions has been described as an "Egg-box" junction.

The application of a membrane separation system in the food industry and in waste water treatment has attracted attention as an energy-saving process. Membrane separation enables a reduction in process costs and CO_2 emissions because latent heat consumption is free for various chemical processes. In addition, recent interest in the use of natural materials has increased due to their biocompatibility and their lack of environment load upon disposal. High-performance membranes made with conventional biomaterials (e.g., cellulose, [16,17] gelatin [18], and chitosan, [15,19]) have been anticipated for use in biocompatible separation [19].

This paper describes the successful preparation of a calcium alginate membrane and demonstrates the role of the mass fraction of α-L-guluronic acid in alginate on the membrane properties. In this study, membrane preparation, mechanical strength, molecular size screening, and the volumetric water fraction of a swollen membrane involved with the mass transfer mechanism of a calcium alginate membrane as it is related to the mass fraction of α-L-guluronic acid were all investigated.

2. Materials and methods

2.1. Materials

Two kind of sodium alginate (grade I-2G and I-2M) were supplied by KIMICA Corporation (Tokyo, Japan). Code I-2G indicates that the major component of the polymer chain was α-L-guluronic acid, while Code I-2M indicates that the major component was β-D-mannuronic acid. Calcium chloride (Anhydrous, 95.0%), urea (60.06 Da), D(+)-glucose (180.16 Da), methyl orange (327.34 Da), and Bordeaux S (604.48 Da) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Indigo carmine (466.37 Da) was purchased from Kokusan Chemical Works, Ltd. (Tokyo, Japan).

2.2. Calibration curve of uronic acid

The calibration curve of uronic acid was based on mass base concentration. Mannuronic acid lactone was used as the standard component of uronic acid. As the standard solution, various concentrations of mannuronic acid lactone were dissolved in water. The concentrations were determined by Bitter-Muir's carbazole sulfuric acid method [20], and the concentration of the colored solution was measured using a spectrophotometer (UV Mini 1240, Shimadzu, Kyoto, Japan). These methods produced good intensity and accuracy of coloration [21].

2.3. Measurement of the mass fraction of homopolymeric blocks of α-L-guluronic acid in sodium alginate

The mass of α-L-guluronic acid in the actual alginate chain was determined by partial hydrolysis combined with Bitter-Muir's carbazole sulfuric acid method. Practical hydrolysis protocols were employed according to a previously published method [21]. Fig. 2 illustrates practical hydrolysis. The actual sodium alginate was separated into three molecular chain blocks (M-G, M-M, and G-G). Fig. 3 presents details of the protocols for practical hydrolysis.

Sodium alginate (0.5 g) was dissolved in 0.3 M HCl (50 ml). The resulting solution was heated in a hot air drying machine (373 K) for 2 h to advance the reaction of practical hydrolysis. The practical hydrolysis solution was then centrifuged (3000 min^{-1}, 15 min), and a sample solution of the M-G block was obtained as the supernatant. The precipitate was mixed with pure water (10 ml), and 3 M NaOH was added to aid dissolution. The concentration was then adjusted to 1% by the addition of pure water, and NaCl was introduced to achieve a 0.1 M concentration of sodium alginate. The solution was adjusted to pH 2.9 using 2.5 M HCl and then centrifuged (3000 min^{-1}, 15 min). The sample solution of the M-M block was obtained as the supernatant. After filtration, the precipitate was mixed with pure water (10 ml) and dissolved by addition of 3 M NaOH, yielding the sample solution of the G-G block. All three sample solutions (M-G, M-M, and G-G) were thus obtained. Their concentrations were determined by Bitter-Muir's carbazole sulfuric acid method using an optical density of 530 nm (UV-1200, Shimadzu, Kyoto, Japan).

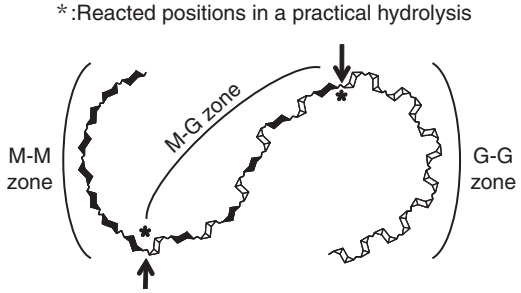

Fig. 2. Image illustrating practical hydrolysis. Sodium alginate was separated into three molecular chain blocks: M-G, M-M, and G-G.

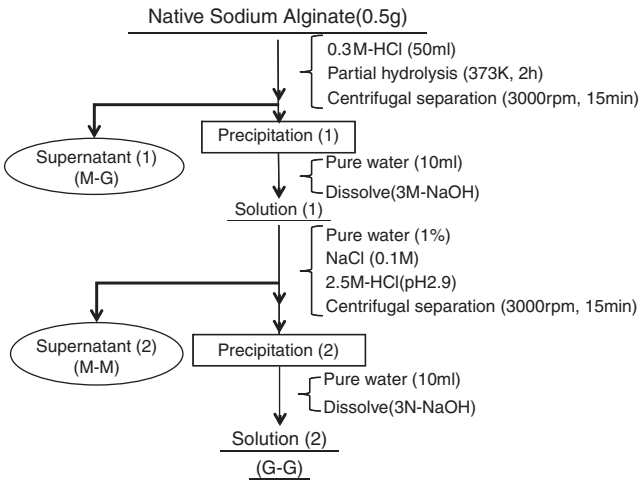

Fig. 3. The protocols used for practical hydrolysis, to measure the mass of each of the three molecular chain blocks (M-G, M-M, and G-G). The concentration of each sample (supernatants (1), and (2) and solution (2)) were determined by Bitter-Muir's carbazole sulfuric acid method.

The mass of the M-G block in the sodium alginate (W_{MG}) was obtained from the concentration of the sample solution of the M-G block. The mass of the M-M block (W_{MM}) and the G-G block (W_{GG}) in the sodium alginate were obtained in the same way. The mass fraction of α-L-guluronic acid in the sodium alginate (F_G) was then calculated using the formula:

$$F_G = \frac{W_{GG} + W_{MG} \times P}{W_{GG} + W_{MG} + W_{MM}} \quad (1)$$

Where P is the partial mass fraction of α-L-guluronic acid in the M-G block. The polymeric structure of the calcium alginate gels was mainly constructed by intermolecular ionic bonds in the homopolymeric blocks of the α-L-guluronic junction zone in combination with Ca^{2+} [7,8]. Therefore, for this study, it is assumed that P is negligible ($P = 0$) (Eq. (2)). Thus, Eq. (1) is rearranged as follows.

$$F_{GG} = \frac{W_{GG}}{W_{GG} + W_{MG} + W_{MM}} \quad (2)$$

The mass fraction of the homopolymeric blocks of α-L-guluronic acid (F_{GG}) was therefore shown to be a key factor in regulating membrane properties.

2.4. Regulation of the mass fraction of homopolymeric blocks of α-L-guluronic acid

F_{GG} was regulated by mixing two different sodium alginates, I-2G (F_{GG}: 0.56) and I-2M (F_{GG}: 0.18). Sodium alginates having three different mass fractions (F_{GG}: 026, 0.35, 0.45) were then prepared. Regulated sodium alginates having five different mass fractions (F_{GG}) were used to prepare the membranes.

2.5. Preparation of calcium alginate membrane

The viscosity range of sodium alginate was adjusted by employing two kind of alginate, I-2G and I-2M. Twenty grams of sodium alginate solution (10 g/l) was placed in a 7 cm-diameter Petri dish. The solution was gradually dried in a desiccator at room temperature (298 K) for one week. A dried thin film of sodium alginate appeared on the Petri dish.

Next, calcium chloride aqueous solution (1 M) was added to the dried thin film of sodium alginate in the Petri dish. A calcium alginate membrane quickly formed in the Petri dish at room temperature. After 20 min, the swollen membrane was separated from the Petri dish and then left in the Petri dish for a further 20 min. The membrane was immersed for a total of 40 min in the calcium chloride aqueous solution.

The formed calcium alginate membrane was then soaked in pure water to remove excess calcium chloride aqueous solution, then stored in pure water.

2.6. Preparation of samples for scanning electron microscopy

The membrane was immersed in liquid nitrogen then dried in a vacuum freeze dryer (RLE-103, Kyowa Vacuum Engineering. Co., Ltd., Tokyo, Japan) (298 K) for 24 h. Prior to analysis, the membrane was coated with a thin layer of Pt, using a sputter-coater (E-1010 Ion Sputter, Hitachi, Ltd., Tokyo, Japan). A scanning electron microscope (Miniscope TM-1000, Hitachi, Ltd.,) was employed to obtain microscopic images.

2.7. Mechanical strength and elastic characteristics

A swollen membrane sample (10 mm wide and 30 mm long) was mounted on a rheometer (CR-DX500, Sun Scientific Co., Ltd., Tokyo, Japan) with a stretching rate of 2 mm/s (298 K). The maximum stress [$N \cdot m^{-2}$] when the membrane ruptured was evaluated based on the loading force divided by the cross-sectional area of the membrane sample. The maximum strain was evaluated as the percentage of critical stretched length when the membrane ruptured divided by the original length of the membrane sample.

2.8. Measurement of mass transfer flux

The overall mass transfer coefficient K_{OL} was determined by measuring the mass transfer flux based on Eqs. (3) and (4). The membrane was sandwiched between twin glass mass transfer cells (Fig. 4), and the set was placed in a thermostatic bath (303 K).

$$\ln\left(1 - \frac{2C_s}{C_{fi}}\right) = -2\frac{A}{V}K_{OL}t \tag{3}$$

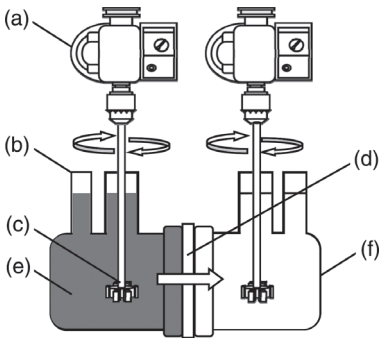

Fig. 4. Diagram showing membrane mass transfer cells. (a) Agitating motor. (b) Mass transfer cell. (c) Impeller. (d) Membrane. (e) Feed solution. (f) Stripping solution.

$$K_{OL}^{-1} = k_{L1}^{-1} + k_m^{-1} + k_{L2}^{-1} \tag{4}$$

Both aqueous phases were sufficiently stirred to create a fully developed turbulent flow. Film mass transfer resistances k_{L1}^{-1} and k_{L2}^{-1} in the overall mass transfer resistance K_{OL}^{-1} were ignored under fully turbulent conditions. In this case, K_{OL} did not depend on the stirring rate. Therefore, it directly indicated the membrane mass transfer coefficient km ($km = D_{eff} \cdot l^{-1}$). The effective diffusion coefficient in the membrane (D_{eff}) was evaluated from km. The initial membrane thickness l was measured with a micrometer (Mitutoyo Corporation, Kanagawa, Japan).

The concentration of the stripping solution was determined by a spectrophotometer (UV Mini 1240, Shimadzu). The absorbances of the color pigments employed (methyl orange, indigo carmine, and Bordeaux S) were measured based on the maximum wavelength (methyl orange 462 nm, indigo carmine 610 nm, and Bordeaux S 520 nm). The concentration of urea (glucose) was determined by the urease-indophenol method (Urea NB, Wako) (mutarotase-GOD method (Glucose C2, Wako)). The absorbance of the colored urea and glucose employed were determined by a spectrophotometer (urea 570 nm, glucose 505 nm).

2.9. Volumetric water fraction of the swollen membrane

The volumetric water fraction of the swollen membrane was not measured directly. Instead, in this study, the volumetric water fraction was evaluated from the mass-based water content (H_M) (Fig. 5). Gravimetric methods were employed to determine the mass-based water content of the swollen membrane (H_M). The swollen membranes had already achieved equilibrium water content. Excess water attached to the membrane surface was removed using filter paper. The masses of the swollen samples (w_e) were measured initially, then,

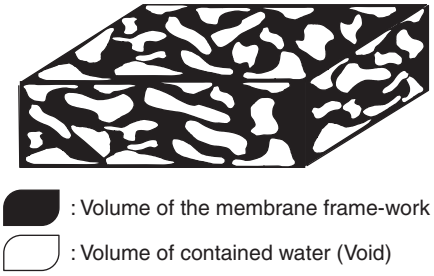

Fig. 5. Image illustrating the volumetric water fraction in the membrane (H_V). The volumetric water fraction of the swollen membrane was evaluated from the mass-based water content in the swollen membrane (H_M) as Eq. (7).

after drying (333 K for 24 h), the masses of the dried membranes (w_d) were measured again. The difference between w_e and w_d indicates the mass of total contained water (w_t):

$$w_t = w_e - w_d \tag{5}$$

The mass-based water content of the swollen membrane (H_M) was then calculated using the following equation:

$$H_M = \frac{w_e - w_d}{w_e} = \frac{w_t}{w_e} \tag{6}$$

The obtained volume of the contained water was w_t/ρ_W. The experimental data of the apparent volume of the swollen membrane was obtained as w_e/ρ_M.

The apparent density of the swollen membrane ρ_M was determined from the mass of the swollen membrane w_e divided by the apparent volume of the swollen membrane. The apparent swollen membrane volume was calculated from the membrane area (square with 4 cm sides) and its thickness. The estimated volumetric water fraction of the swollen membrane (H_V) was calculated using Eq. (7).

$$H_V = \frac{(w_t/\rho_w)}{(w_e/\rho_M)} \tag{7}$$

3. Results and discussion

3.1. Scanning electron microscope images

No pores for mass transfer could be observed in a scanning electron microscope image. The higher F_{GG} membrane had a dense appearance (Fig. 6a), whereas the lower F_{GG} membrane appeared more coarse (Fig. 6b). The appearance of both F_{GG} membranes was smoothened by increasing the calcium chloride as a cross-linker (Figs. 6c, d).

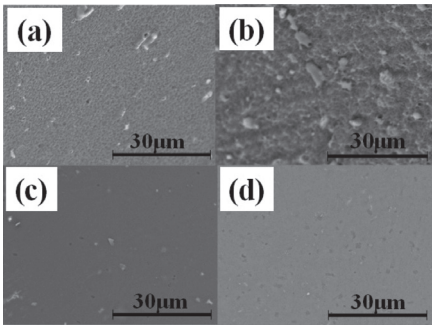

Fig. 6. SEM images of the surface of the calcium alginate membrane. (a) Homopolymeric block with higher guluronic acid content (F_{GG} 0.56, $CaCl_2$ 0.1 M). (b) Homopolymeric block with higher mannuronic acid content (F_{GG} 0.18, $CaCl_2$ 0.1 M). (c) Homopolymeric block with higher guluronic acid content (F_{GG} 0.56, $CaCl_2$ 1.0 M). (d) Homopolymeric block with higher mannuronic acid content (F_{GG} 0.18, $CaCl_2$ 1.0 M.) (× 2500).

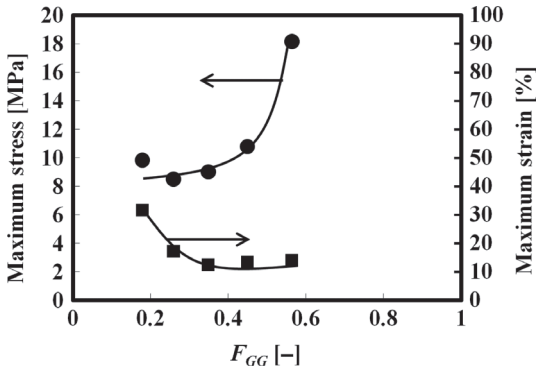

Fig. 7. Effect of F_{GG} on the maximum stress and strain values of the calcium alginate membrane at membrane rupture. •: Maximum stress. ■: Maximum strain.

3.2. Mechanical strength and elastic characteristics

Fig. 7 depicts the correlation of maximum stress and maximum strain at membrane rupture. The mechanical strength and elastic characteristics apparently changed with F_{GG}. The maximum stress increased with increasing F_{GG}. Mechanical strength was increased by cross-linking, especially when combined with higher F_{GG}. In contrast, the maximum strain when the membrane ruptured was remarkably reduced by increasing F_{GG}. The polymeric framework of the calcium alginate became more densely populated with a higher calcium chloride concentration [22]. Increasing F_{GG} obviously enhanced the polymeric framework of the membrane.

3.3. Mass transfer flux

The molecular size screening effect was investigated by measuring mass transfer flux using various molecular size

indicators (Urea 60 Da, Glucose 180 Da, Methyl Orange 327 Da, Indigo Carmin 466 Da, and Bordeaux S 604 Da). Superior molecular size screening performance was established in our tested range (Fig. 8). The result strongly suggests that the mass transfer channel was considerably mono-disperse in our experimental range of molecular sizes [22], something that has not been previously reported. Molecular size screening evidently appeared in a lower molecular range than glucose, especially for higher values of F_{GG}. The diffusion coefficient in bulk aqueous phase D was plotted for comparison. The large dependence of effective diffusion coefficient on molecular size indicates that the polymeric framework of a calcium alginate membrane is sensitive to mass transfer.

Fig. 9 illustrates the effect of F_{GG} on the effective diffusion coefficient of urea. The effective diffusion coefficient gradually decayed due to the progressive cross-linking of molecular frameworks within the membrane. The polymeric structure of calcium alginate gels was mainly governed by the intermolecular ionic bonds with homopolymeric blocks of the α-L-guluronic acid junction zone in combination with Ca^{2+} [7,8]. The calcium chloride acted as a cross-linker of molecular frameworks in the alginate molecular chain.

3.4. Volumetric water fraction of the swollen membrane

The volumetric water fraction (H_V) of the swollen membrane decreased linearly with increasing F_{GG}, as shown in Fig. 10.

Fig. 11 illustrates the correlation of the volumetric water fraction of the swollen membrane with the effective diffusion coefficient of urea. The effective diffusion coefficient and the volumetric water fraction were restrained by increasing F_{GG}. The good correlation between the volumetric water fraction and the effective diffusion coefficient contributed to understanding of the mass transfer channel of the alginate membrane. The mass transfer channel was governed by the mass fraction of homopolymeric blocks of α-L-guluronic acid (F_{GG}). These "Egg-box" junction zones regulated the mass transfer mechanism of the alginate membrane.

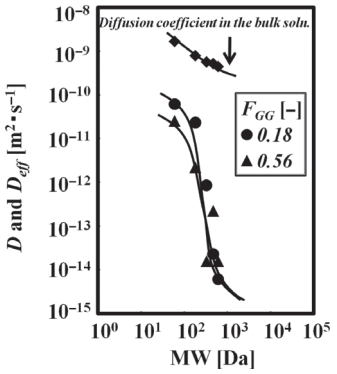

Fig. 8. The effective diffusion coefficient was changed remarkably in our experiment as molecular size increased from 60 Da to 600 Da. The symbol ■ indicates the diffusion coefficient in a bulk aqueous solution, based on the Wilke-Chang equation. Temperature: 303 K. Agitation rate: 850 min^{-1}.

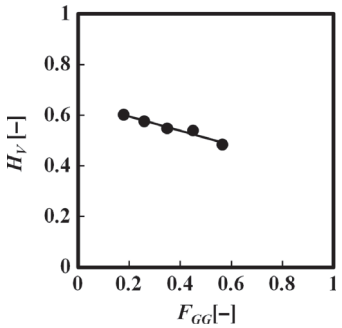

Fig. 10. Effect of F_{GG} on the volumetric water fraction of the swollen membrane. The volumetric water fraction in swollen state was evaluated from the mass mass-based water content as Eq. (7).

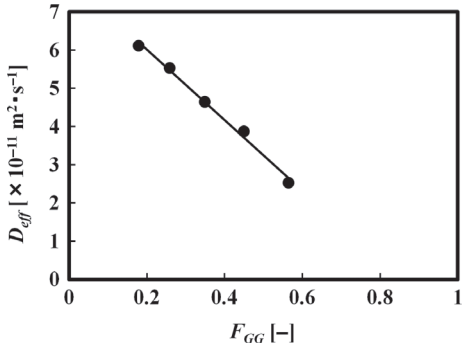

Fig. 9. Effect of F_{GG} on the effective diffusion coefficient of urea.

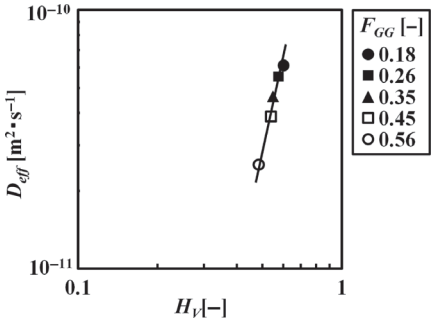

Fig. 11. Correlation of the volumetric water fraction of the swollen membrane with the effective diffusion coefficient of urea.

Chen and Lostrito (1996) pointed out in their paper that ln (D_{eff}/D) was linearly proportional to (H_V^{-1}–1) [23]. This is applicable to highly swollen hydrogel membranes, and is consistent with the opinion of Vadalkar et al. (1993) [24]. It is also applicable to very water soluble solutes. These two points ("highly swollen hydrogel membrane" and "very water soluble solutes") were incorporated into our experimental conditions. A detailed discussion of this was presented by Yasuda et al. (1971) [25]. According to their paper, ln (D_{eff} / D) was correlated linearly with (H_V^{-1}–1). The dependence of the effective diffusion coefficient of a swollen polymer membrane can usually be explained by Yasuda's free volume theory [25]:

$$\ln D_{eff} = \ln D - \frac{b(1-a)x}{1+ax} \tag{8}$$

Eq. (8) was rearranged as follows:

$$\ln\left(\frac{D_{eff}}{D}\right) = -\frac{b(1-a)x}{1+ax} \tag{9}$$

Where $x = (H_V^{-1}–1)$, $a = V_{fm}/V_{fl}$, $b = V^*/V_{fl}$, D_{eff} and D are the effective diffusion coefficient in the membranes and in bulk solvent, respectively. H_V is the volumetric water fraction of the swollen membrane and a is the free volume ratio of the dry membrane (V_{fm}) to that of solvent (V_{fl}), while b is the volumetric ratio of the permeant characteristic volume (V^*) to the free volume in the solvent (V_{fl}). It is apparent from Eq. (9) that the ln (D_{eff} / D) is not represented by the linear function of the volumetric water fraction in the swollen membrane (H_V). As two special cases of Eq. (9), first, the ln (D_{eff} / D) becomes independent of membrane swelling at low H_V ($x \to \infty$). The left hand term of Eq.(9) becomes almost constant. Second, for a region of high H_V ($x \to 0$), the ln (D_{eff} / D) is linearly proportional to x and presents a negative slope of b(1–a).

Fig. 12 investigates the ln (D_{eff} / D) of urea in a calcium alginate membrane in the swollen state based on the free volume theory, Eq. (9). A plot of ln (D_{eff} /D) vs. x was applied to the higher volumetric water fraction. The correlation agreed well with the second case mentioned above (high H_V). The ln (D_{eff} / D) is linearly proportional to x and presents a negative slope of b (1- a). The intercept of the ordinate indicates that the effective diffusion coefficient approaches the diffusion coefficient of the bulk phase at a higher volumetric water fraction of the swollen state membrane. This was in agreement with Yasuda's discussions and Chen and Lostrito's presentation [23]. Vadalkar et al. (1993) presented a good correlation of ln (D_{eff}/ D) vs. x. Their trend also agreed with our experimental results.

The effective diffusion coefficient in the membrane can be presented by the following equation.

$$D_{eff} = \frac{D\,\varepsilon}{\tau} \tag{10}$$

Where, ε is the void fraction. τ is tortuosity of the membrane. In this work, the void fraction was assumed to be the volumetric water fraction of the swollen membrane (H_V). Eq. (10) was therefore rearranged as follows:

$$D_{eff} = \frac{D\ H_V}{\tau} \tag{11}$$

D_{eff} and H_V were determined independently from our experiments. Therefore, τ was estimated from Eq. (12).

$$\tau = \frac{D\ H_V}{D_{eff}} \tag{12}$$

The change of τ with F_{GG} is presented in Fig. (13). Tortuosity increased from 16 to 32 with increasing F_{GG}, which changed from 0.18 to 0.56. This trend indicated that the mass fraction of α-L-guluronic acid was the

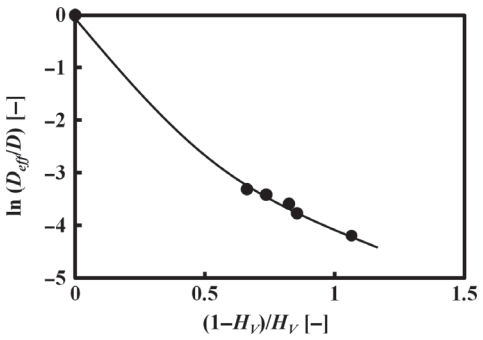

Fig. 12. Effective diffusion coefficient of urea in calcium alginate membrane regulated by F_{GG}. Test of free volume theory.

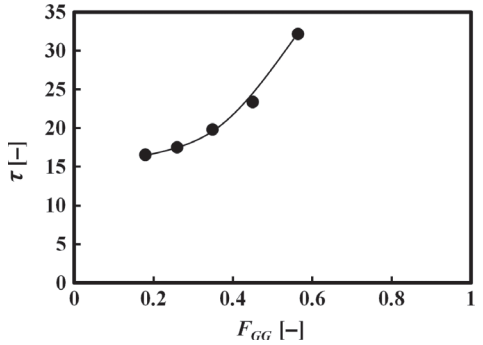

Fig. 13. Effect of F_{GG} on the tortuosity. Contribution of "Egg-box" junction structure to tortuosity.

dominant factor our regulating of tortuosity. The detail reason for high level of tortuosity is not clear at present. Other factors inhibiting diffusion in the membrane could be illustrated, e.g., adsorption on the polymer network or molecular affinity between alginate polymer chains and the molecules tested.

4. Conclusion

The impact of α-L-guluronic acid on the mass transfer character of calcium alginate membranes was demonstrated, not only on the effective diffusion coefficient but also on the mechanical strength of the membrane. A membrane was successfully prepared with various mass fractions of α-L-guluronic acid in sodium alginate. The volumetric water fraction of the swollen membrane decreased with increasing F_{GG}. The effective diffusion coefficient of smaller molecules apparently decreased with increasing mass fraction of α-L-guluronic acid. The results suggest that increasing F_{GG} dominantly governs the polymeric framework of calcium alginate membranes. This original finding on the impact of F_{GG} has the potential to enable preparation of calcium alginate membranes with any desirable molecular size screening function.

Acknowledgements

The authors are sincerely grateful to KIMICA Corporation (Tokyo, Japan) for kind providing sodium alginates samples, I-2M and I-2G. The authors are sincerely grateful to Prof. Dr. Hirosi Anzai of Nihon University, who kindly provided much useful advice for determining the F_{GG} in sodium alginate. The SEM image was obtained byDr. Kei Tao of Nihon University. The authors appreciate his technical support.

Symbols

A — Area of membrane [m^2].
a — The ratio of the free volume of the dry membrane (V_{fm}) to the free volume of solvent (V_{fl}) [-].
b — The ratio of the permeant characteristic volume (V^*) to the free volume in the solvent (V_{fl}) [-]
C_{fi} — Initial concentration in the feed solution [M].
C_s — Concentration in the stripping solution [M].
D — Diffusion coefficient estimated from an empirical equation in a bulk aqueous phase [$m^2 \cdot s^{-1}$].
D_{eff} — Effective diffusion coefficient measured [$m^2 \cdot s^{-1}$].
F_G — Mass fraction of α-L-guluronic acid in sodium alginate determined by Eq. (1) [-].
F_{GG} — Mass fraction of homopolymeric blocks of α-L-guluronic acid in sodium alginate determined by Eq. (2) [-].
H_M — The mass-based water content at swollen membrane [-], defined by Eq. (6).
H_V — The volumetric water fraction at swollen membrane [-], defined by Eq. (7).
K_{OL} — Overall mass transfer coefficient [$m \cdot s^{-1}$].
K_{OL}^{-1} — Overall mass transfer resistance [$(m \cdot s^{-1})^{-1}$].
k_m — Membrane mass transfer coefficient [$m \cdot s^{-1}$].
k_{L1} — Film mass transfer coefficient in the feed phase [$m \cdot s^{-1}$].
k_{L2} — Film mass transfer coefficient in the stripping phase [$m \cdot s^{-1}$].
l — Membrane thickness in the initial state [m].
P — Partial mass fraction of α-L-guluronic acid in M-G block [-].
t — Time [s].
V — Volume of aqueous solution in the transfer cell presented in Fig. 4. [m^3].
V^* — The permeant characteristic volume [m^3].
V_{fl} — The free volume of the solvent [m^3].
V_{fm} — The free volume of the dry membrane [m^3].
W_{GG} — Mass of G-G block in sodium alginate [kg].
W_{MG} — Mass of M-G block in sodium alginate [kg].
W_{MM} — Mass of M-M block in sodium alginate [kg].
w_e — Initial mass of the swollen membrane [kg].
w_d — Mass of dried membrane [kg].
w_t — Mass of total contained water [kg].
x — The ratio of the framework fraction to void fraction of the membrane (H_V^{-1}–1) [-].
ε — Void fraction of the membrane [-].
ρ_M — Density of the swollen membrane [$kg \cdot m^{-3}$].
ρ_W — Density of pure water [$kg \cdot m^{-3}$].
τ — Tortuosity of the membrane [-], defined by Eq. (12).

References

[1] T.N. Julian, G.W. Radebaugh and S.J. Wisniewski, Permeability characteristics of calcium alginate films, J. Controlled Release, 7 (1988) 165–169.
[2] A. Haug, B. Larsen and O. Smidsrod, Uronic acid sequence in alginate from different sources, Carbohydr. Res., 32 (1974) 217–225.
[3] Y. Ye, P.L. Clech, V. Chen, A.G. Fane and B. Jefferson, Fouling mechanisms of alginate solutions as model extracellular polymeric substances, Desalination, 175 (2005) 7–20.
[4] M. Strathmann, J. Wingender and H.-C. Flemming, Application of fluorescently labelled lectins for the visualization and biochemical characterization of polysaccharides in biofilms of *Pseudomonas aeruginosa*, J. Microbiol. Methods., 50 (2002) 237–248.

[5] S. Lee, W.S. Ang and M. Elimelech, Fouling of reverse osmosis membranes by hydrophilic organic matter: implications for water reuse, Desalination, 187 (2006) 313–321.
[6] K. Katsoufidou, S.G. Yiantsios and A.J. Karabelas, Experimental study of ultrafiltration membrane fouling by sodium alginate and flux recovery by backwashing, J. Membr. Sci., 300 (2007) 137–146.
[7] P. Gacesa, Alginates, Carbohydrate Polymers, 8 (1988) 161–182.
[8] G.T. Grant, E.R. Morris, D.A. Rees, P.J.C. Smith and D. Thom, Biological interactions between polysaccharides and divalent cations: The Egg-Box model, FEBS Lett., 32, No. 1 (1973) 195–198.
[9] P.F. Almeida and A.J. Almeida, Cross-linked alginate–gelatine beads: a new matrix for controlled release of pindolol, J. Controlled Release, 97 (2004) 431–439.
[10] Z. Konsoula and M. Liakopoulou-Kyriakides, Starch hydrolysis by the action of an entrapped in alginate capsules α-amylase from *Bacillus subtilis*, Process Biochem., 41 (2006) 343–349.
[11] R. Dembczynski and T. Jankowski, Characterisation of small molecules diffusion in hydrogel-membrane liquid-core capsules, Biochem. Eng. J., 6 (2000) 41–44.
[12] G.R. Castro, R.R. Kamdar, B. Panilaitis and D.L. Kaplan, Triggered release of proteins from emulsan–alginate beads, J. Controlled Release, 109 (2005) 149–157.
[13] J. Hubble and J.D. Newman, Alginate Ultrafiltration Membranes, Biotechnol. Lett., 7, No. 4 (1985) 273–276.
[14] C.P. Athanasekou, S.K. Papageorgiou, V. Kaselouri, F.K. Katsaros, N.K. Kakizis, A.A. Sapalidis and N.K. Kanellopoulos, Development of hybrid alginate/ceramic membranes for Cd^{2+} removal, Microporous Mesoporous Mater, 120 (2009) 154–164.
[15] A.S. Reddy, S. Kalyani, N.S. Kumar, V.M. Boddu and A. Krishnaiah, Dehydration of 1,4-dioxane by pervaporation using crosslinked calcium alginate-chitosan blend membranes, Polym. Bull., 61 (2008) 779–790.
[16] A.M. Sokolnicki, R.J. Fisher, T.P. Harrah and D.L. Kaplan, Permeability of bacterial cellulose membranes, J. Membr. Sci., 272 (2006) 15–27.
[17] M. Zhao, X.-L. Xu, Y.-D. Jiang, W.-Z. Sun, W.-F. Wang and L.-M. Yuan, Enantioseparation of trans-stilbene oxide using a cellulose acetate membrane, J. Membr. Sci., 336 (2009) 149–153.
[18] A. Bigi, G. Cojazzi, S. Panzavolta, N. Roveri and K.Rubini, Stabilization of gelatin films by crosslinking with genipin, Biomaterials, 23 (2002) 4827–4832.
[19] T. Takahashi, M. Imai and I. Suzuki, Water permeability of chitosan membrane involved in deacetylation degree control, Biochem. Eng. J., 36 (2007) 43–48.
[20] T. Bitter and H.M. Muir, A modified uronic acid carbazole reaction, Anal. Biochem., 4 (1962) 330–334.
[21] H. Anzai, N. Uchida and E. Nishide, Comparative studies of colorimetric analysis for uronic acids, Bull. Coll. Agr. & Vet. Med. Nihon Univ., No. 43 (1986) 53–56.
[22] K. Kashima, M. Imai and I. Suzuki, Superior molecular size screening and mass-transfer characterization of calcium alginate membrane, Desalin. Water Treat., 17 (2010) 143–149.
[23] S.X. Chen and R.T. Lostritto, Diffusion of benzocaine in poly (ethylene-vinyl acetate) membranes: Effects of vehicle ethanol concentration and membrane vinyl acetate content, J. Controlled Release, 38 (1996) 185–191.
[24] V.S. Vadalkar, M.G. Kulkarni and S.S. Bhagwat, Anomalous sorption of binary solvents in glassy polymers: interpretation of solute release at constant rates, Polymer, 34(20) (1993) 4300–4306.
[25] H. Yasuda, C.E. Lamaze and A. Peterlin, Diffusive and hydraulic permeabilities of water in water-swollen polymer membranes, J. Polymer Science: Part A–2, 9 (1971) 1117–1131.