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Evaluation of A Novel Ion-Exchange Resin, St-60 with A Cross-Linking Degree of 40% and Various Numbers of Methylene Groups in the Porous Shell

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ABSTRACT

The complex relationship between the molecular structure of ion-exchange resins and the elution of carbohydrates presents a challenge for the development of polymer materials for high-performance liquid chromatography under a wide range of conditions. We evaluated the effect of the number of methylene groups in the functional chain of the shell portion on carbohydrate separation. In particular, core-shell ion-exchange resins with a monomer weight ratio of 40:60 (denoted as St-60) were synthesized with a constant cross-linking degree of 40%. The number of methylene groups in the functional chain of the porous polymer shell was varied from two to six for analyses of carbohydrate separation performance under strong alkaline conditions. A mixture of inositol, glucose, fructose, and sucrose was separated using a 0.10 or 0.15 mol/L NaOH eluent at flow rates of 0.3–0.7 mL/min. As the number of methylene groups increased, the carbohydrate retention times for St-60(Me:4) at flow rates of 0.3–0.7 mL/min with 0.10 mol/L NaOH eluent increased slightly. The theoretical plate numbers of glucose and fructose at flow rates of 0.5 and 0.7 mL/min decreased as the number of methylene groups decreased from six to two. These results suggest that St-60 core-shell ion-exchange resins are highly efficient for carbohydrate analyses. Their suitability for strongly alkaline conditions allows their effective use in electrochemical detection.

Keywords

High-performance liquid chromatography, Core-shell ion-exchange resin, Carbohydrates, Retention time, Theoretical plate number, Density-Function theory, Hartree-Fock.

Introduction

Choosing an appropriate ion-exchange resin is essential for high-performance liquid chromatography (HPLC), a critical analytical tool. Various core-shell resins have been developed for this purpose [1,2]; however, the exchange capacity of resins is often limited under particular conditions. For example, silica-based resins, such as octadecyl-functionalized silica resins [3-8], are not suitable for use under strongly alkaline conditions. Styrene-divinylbenzene- and acrylamide-type polymers, frequently used as base materials for organic resins [9-13], are limited for applications in high-speed HPLC owing to their fully porous structure.

To solve these problems, core-shell ion-exchange resins composed of a porous polymer shell and dense core have been synthesized. These resins provide superior durability at high pH. Two commercially available examples are core-shell ion-exchange resins prepared via precipitation polymerization around the core [14,15] and latex-type resins using a styrene base [16-18].

The performance of these resins is mainly determined by the thickness and degree of cross-linking of the shell portion; therefore, these parameters should be optimized for HPLC analyses [19]. Because the retention time increases with the thickness of the porous shell, the shell portion should be as thin as possible to reduce the analysis time. Furthermore, an appropriate degree of cross-linking in the porous shell portion is necessary for good separation performance.

We have previously investigated the effects of various factors (shell thickness, degree of cross-linking in the porous shell, concentration of the NaOH eluent, and number of methylene groups in the functional chain) on the performance of core-shell ion-exchange resins consisting of a dense polymer core and a porous polymer shell with a functional chain in the polymer structure [19-27]. We initially demonstrated that ion-exchange resins with a core-shell monomer weight ratio (before suspension polymerization) of 20:80 (St-80) and a cross-linking degree of 55% in the porous region had a shorter retention time in HPLC analyses of carbohydrates than that of the fully porous resin (0:100) [28-30]. We also evaluated St-80 resins with various degrees of cross-linking (i.e., 10%, 40%, and 55%) in the porous shell [31] and with a constant cross-linking degree of 55% and core-shell monomer weight ratios of 50:50, 40:60, and 30:70 (St-50, St-60, and St-70, respectively), which affected the shell thickness [32].

We then evaluated the carbohydrate elution behavior using St-50 and St-70 ion-exchange resins with cross-linking degrees of 10%, 40%, and 55% [33,34] and using St-60, St-70, and St-80 resins with two, four, and six methylene groups in the functional chain (denoted as St-60(55% Me:2, 4, and 6), St-70(55% Me:2, 4, and 6), and St-80(55% Me:2, 4, and 6)), holding the cross-linking degree constant at 55% [35-37].

Resins reported to date typically have a crosslinking degree of 55%. The effects of reducing the degree of cross-linking on carbohydrate separation are not clearly established. In this study, we evaluated the carbohydrate elution behavior using St-60 (monomer weight ratio: 40:60) with a cross-linking degree of 40% in the porous shell and two, four, or six methylene groups (denoted as St-60(40% Me:2), St-60(40% Me:4), and St-60(40% Me:6), respectively). This study provides insight into the factors contributing to carbohydrate elution behavior and provide a basis for optimizing resins with respect to methylene groups.

Materials and Methods

Materials

myo-Inositol, sucrose, and NaOH were obtained from Fujifilm Wako Chemicals Co. (Richmond, VA, USA). D(−)-Fructose and D(+)-glucose were obtained from Kanto Chemical Co. (Tokyo, Japan). Ultrapure water (ELGA) was used to prepare the eluent and sample solutions. Sample solutions were prepared by sequentially mixing and diluting the stock solutions to concentrations of 500 or 1000 mg/L.

Preparation of core–shell ion-exchange resins

The core-shell ion-exchange resin consisted of a hard polymer core and a porous shell containing functional chains, as shown in Figures 1 and 2 [31]. The porous shell was synthesized by reacting a chloromethylstyrene-divinylbenzene copolymer carrier with a tertiary amine, as described previously [19].

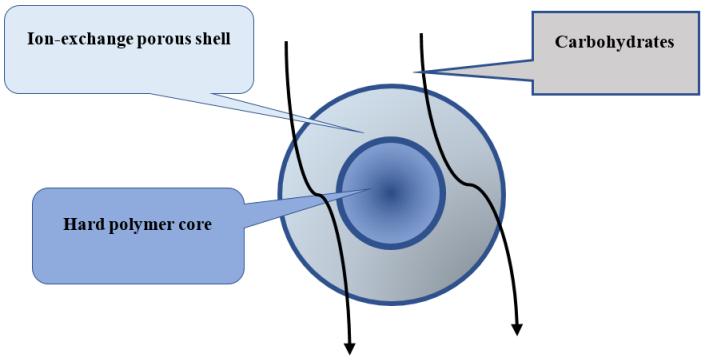


Figure 1: Structure of the core–shell ion-exchange resin consisting of a dense polymer core and an ion exchange porous polymer shell.

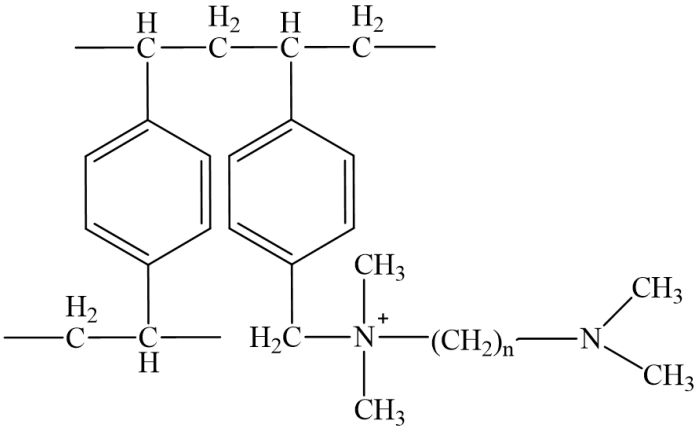


Figure 2: Chemical structure of the porous polymer in the ion-exchange resin shell (n = 2, 4, and 6).

The thickness of the shell was kept constant by maintaining a constant core-shell monomer weight ratio of 40:60 and a constant total mass of monomers. The degree of cross-linking in the porous layer was also kept constant at 40% by employing a styrene/divinylbenzene weight ratio of 60:40 [32]. The number of methylene groups in the functional chain of the porous layer was adjusted using *N*,*N*,*N*′,*N*′-tetramethyl ethylenediamine, *N*,*N*,*N*′,*N*′-tetramethyl-1,4-butanediamine, and *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexamethylenediamine as tertiary amines to produce core-shell ion-exchange resins with two, four, and six methylene groups (denoted as St-60(40% Me:6), St-60(40% Me:4), and St-60(40% Me:2), respectively). For comparison, a fully porous resin (i.e., with no core) with a degree of cross-linking of 40% and six methylene groups in the functional chain was prepared by reacting the chloromethylstyrene–divinylbenzene copolymer carrier (divinylbenzene weight ratio: 40%) with the *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexamethylenediamine tertiary amine (denoted as Fully(40% Me:6)). The prepared resins had an average diameter of 5 μm. We prepared 3 g of each core-shell and fully porous resin.

HPLC Analysis Conditions

HPLC was performed using a DKK-TOA SU-300 instrument equipped with an electrochemical detector and gold electrode. The resins were mixed with 10 mL of a 0.10 mol/L NaOH eluent and

packed into a 4.6 mm × 150 mm I.D. stainless steel column using a conventional slurry packing method at a constant pressure of 120 kg/cm^2. The sample solution (20 µL) containing carbohydrates (inositol, glucose, fructose, and sucrose) was injected into an AS-8020 HPLC autosampler (Tosoh, Tokyo, Japan) and eluted with either a 0.10 or 0.15 mol/L NaOH eluent at room temperature (30 °C). Flow rates of 0.3, 0.5, and 0.7 mL/min were used. The theoretical plate number (*N*) of each carbohydrate in the standard solution was determined using a built-in data-processing program. We calculated the electrostatic charge on the N^+ atom in the functional chain and the configuration using model compounds by density functional theory using the ωB97X-D density functional and 6.31G* basis set in Spartan'20 (Figure 3).

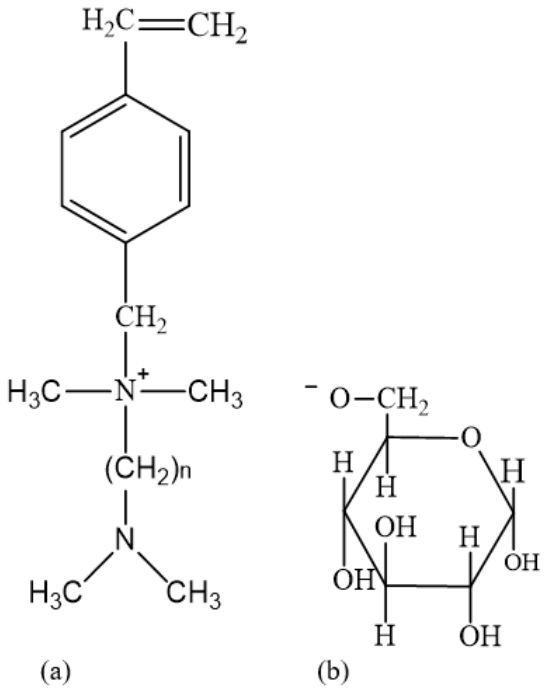


Figure 3: Structures used for optimization of the electrostatic charge on the N+ atoms in the functional chain using Spartan'20: (a) functional chain of the ion-exchange resin and (b) representative carbohydrate molecule.

Results

Carbohydrate separation performance of St-60(40% Me:2), St-60(40% Me:4), and St-60(40% Me:6) ion-exchange resins

Effects of the NaOH eluent concentration and flow rate

We evaluated the retention times of glucose, fructose, and sucrose using a 0.10 mol/L NaOH eluent and St-60(40% Me:2), St-60(40% Me:4), and St-60(40% Me:6) core-shell ion-exchange resins, which had a core-shell monomer weight ratio of 40:60 and two, four, and six methylene groups, respectively.

We evaluated the carbohydrate separation performance of columns packed with St-60(40% Me:2, 4, and 6) using a 0.10 mol/L NaOH eluent at flow rates of 0.3, 0.5, and 0.7 mL/min (Table 1). Figure 4a–f presents the chromatograms of St-60(40% Me:6 and 4) at flow rates of 0.3, 0.5, and 0.7 mL/min. The carbohydrate separation performance of columns packed with the St-60(55% Me:6) resins using a 0.10 mol/L NaOH eluent at flow rates of 0.3, 0.5, and 0.7 mL/min is shown in Table 1. Figure 5a–c presents the retention times of glucose, fructose, and sucrose at flow rates of 0.3, 0.5, and 0.7 mL/min with 0.10 NaOH eluent.

Table 1: Retention times (min) of glucose, fructose, and sucrose using St-60(40% CH_2-2, 4, and 6) with 0.10 mol/L NaOH eluent at flow rates of 0.3, 0.5, and 0.7 mL/min.

Flow rate	Number of CH_2 groups	Glu		Fru		Suc	
(mL/min)	Cross-linking	40%	55%	40%	55%	40%	55%
0.3	2	13.2	16.5	14.3	19.0	15.3	22.3
	4	19.4	17.2	21.9	19.6	24.2	23.1
	6	19.6	16.9	21.8	20.2	25.8	23.8
	Fully porous, 6	34.9	26.9	43.5	32.5	58.6	44.2
0.5	2	8.0	10.0	8.7	11.5	9.3	13.5
	4	11.8	10.4	13.2	11.8	14.7	13.8
	6	12.0	10.1	13.4	11.9	15.9	14.1
	Fully porous, 6	21.1	16.4	26.6	19.6	35.5	27.2
0.7	2	6.8	7.2	7.3	8.3	7.9	9.8
	4	8.5	7.5	9.5	8.5	10.7	10.2
	6	8.8	7.0	9.8	8.2	11.5	9.6
	Fully porous, 6	15.3	16.4	19.2	19.6	25.7	27.2

Each carbohydrate for St-60(40% Me:4 and 6) showed longer retention times than those of St-60(55% Me:4 and 6) at flow rates of 0.3, 0.5, and 0.7 mL/min with 0.10 mol/L NaOH eluent. A similar trend was observed for Fully (40% Me:6) at flow rates of 0.3 and 0.5 mL/min. The chromatograms of St-60(55% Me:6) showed clean peaks, as shown in Figure 5a–c [35]. Next, the eluent concentration was increased to 0.15 mol/L NaOH. The retention times of glucose, fructose, and sucrose for St-60(40% Me: 2, 4, and 6) and St-60(55% Me:2, 4, and 6) at flow rates of 0.3, 0.5, and 0.7 mL/min are listed in Table 2.

Table 2: Retention times (min) of glucose, fructose, and sucrose using St-60(40% CH_2-2, 4, and 6) with 0.15 mol/L NaOH eluent at flow rates of 0.3, 0.5, and 0.7 mL/min.

Flow rate	Number of CH_2 groups	Glu		Fru		Suc	
(mL/min)	Cross-linking	40%	55%	40%	55%	40%	55%
0.3	2	11.2	13.3	11.9	15.0	13.0	17.7
	4	16.2	13.6	17.9	15.3	21.5	17.5
	6	18.5	13.8	21.3	15.9	27.7	18.6
	Fully porous, 6	26.7	26.9	33.2	32.5	46.1	44.2
0.5	2	6.8	8.1	7.3	9.1	7.9	10.9
	4	9.9	8.2	10.8	9.2	13.3	10.6
	6	11.4	8.4	13.0	9.7	12.0	11.3
	Fully porous, 6	16.3	16.4	20.1	19.6	28.3	27.2
0.7	2	5.0	5.9	5.3	6.6	5.8	7.9
	4	7.2	6.0	7.9	6.7	9.6	7.6
	6	8.3	6.1	9.5	7.0	12.3	8.2
	Fully porous, 6	11.8	16.4	14.5	19.6	21.1	27.2

Glucose, fructose, and sucrose for St-60(40% Me:4 and 6) at flow rates 0.3, 0.5, and 0.7 mL/min with 0.15 mol/L NaOH eluent

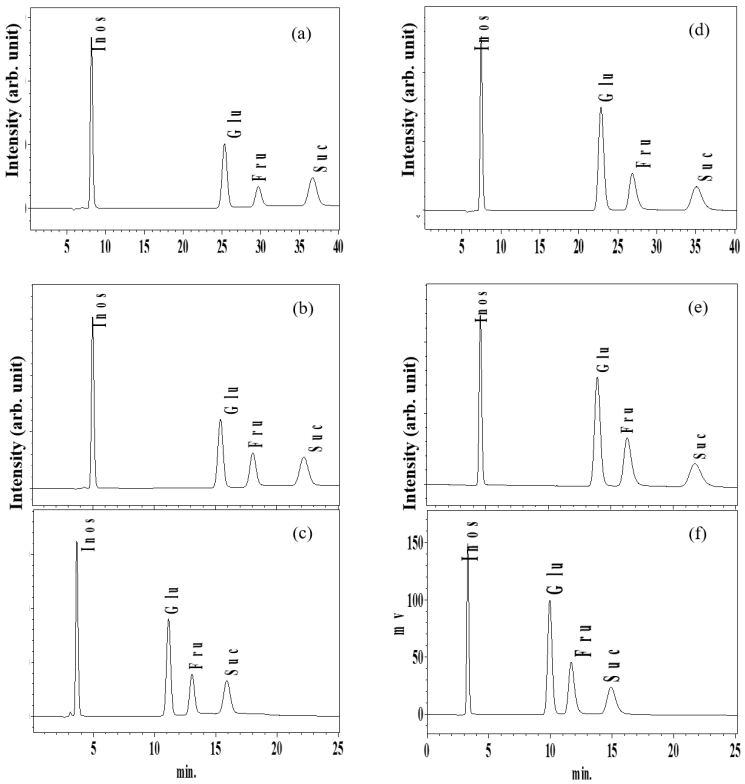


Figure 4a-f: Chromatograms obtained for the separation of inositol, glucose, fructose, and sucrose using St(40% Me-6) with a 0.1 mol/L NaOH (a) 0.3 l/min, (b) 0.5 ml/min, (c) 0.7 ml/min, and using St(40% Me-4) (d) 0.3 ml/min, (e) 0.5 ml/min, (f)0.7 ml/min.

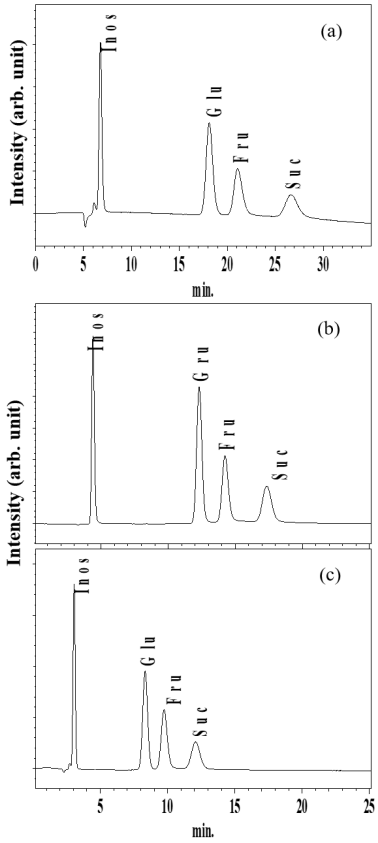


Figure 5a-c: Chromatograms obtained for the separation of inositol, glucose, fructose, and sucrose using St(55% Me-6) with a 0.1 mol/L NaOH (a) 0.3 ml/min, (b) 0.5 ml/min, (c) 0.7 ml/min.

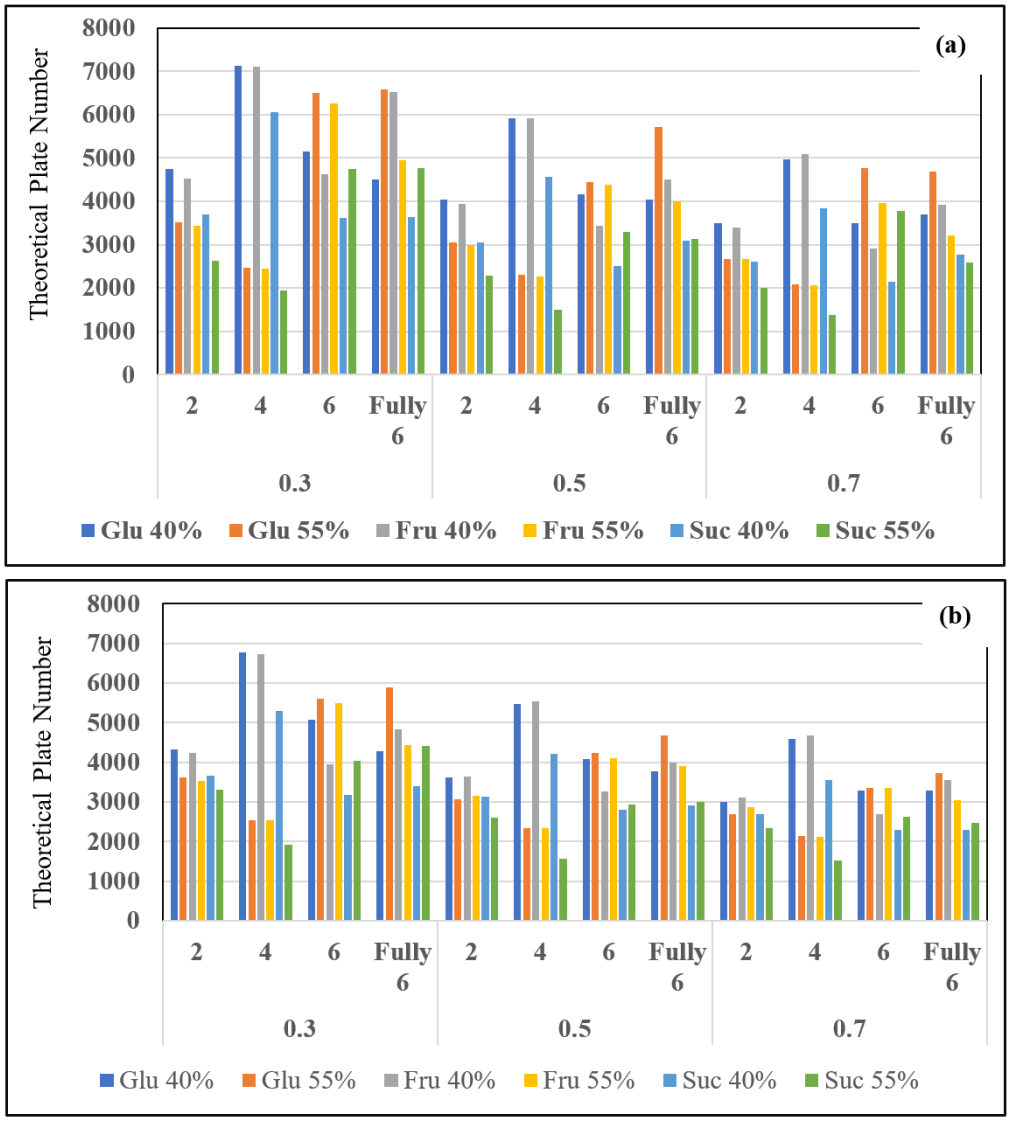


Figure 6: Theoretical plate numbers *N* of glucose, fructose, and sucrose using St-60(40% Me:2), St-60(40% Me:4), St-60(40% Me:6, and Fully(40% Me:6) with (a) 0.10 mol/L and (b) 0.15 mol/L NaOH eluents at flow rates of 0.3, 0.5, and 0.7 mL/min.

showed longer retention times than those of St-60(55% Me:4 and 6). Glucose, fructose, and sucrose for St-60(40% Me:2) showed the opposite trend, i.e., retention times were shorter than those for St-60 (55% Me:2).

Glucose, fructose, and sucrose for Fully (40% Me:6) showed longer retention times than those of Fully (55% Me:6) at flow rates of 0.3 and 0.5 mL/min with the 0.10 mol/L NaOH eluent (Table 1). The retention times of glucose and fructose for Fully (40% Me:6) and Fully (55% Me:6) were nearly the same at flow rates of 0.3 and 0.5 mL/min with the 0.15 mol/L NaOH eluent (Table 2). Glucose, fructose, and sucrose for Fully (40% Me:6) with 0.15 M NaOH eluent at a flow rate of 0.7 mL/min showed smaller retention times than those of Fully (55% Me:6).

Resolution Between Glucose and Fructose Peaks

To further investigate the carbohydrate-separation performance of the resins, we evaluated the resolution between the glucose and fructose peaks (Table 3), which were adjacent in the chromatograms. When using the 0.10 mol/L NaOH eluent, resolutions of ≥1.5 were achieved for the St-60(40% Me:4 and 6) core-shell resins at flow rates of 0.3 and 0.5 mL/min, indicating that they had good separation performance. Those of St-60 (40% Me:2) were 1.2, 1.1, and 1.0 at flow rates of 0.3, 0.5, and 0.7 mL/min, respectively. When using the 0.15 mol/L NaOH eluent, the resolution for St-60 (40% Me:4 and 6) core-shell resins showed similar results to those obtained using the 0.10 mol/L NaOH eluent.

When using Fully (40% Me:6) with the 0.10 mol/L NaOH eluent, the resolutions between the glucose and fructose peaks were 3.4, 3.0, and 3.0 at flow rates of 0.3, 0.5, and 0.7 mL/min, respectively, indicative of good separation performance. When using Fully (40% Me:6) with the 0.15 mol/L NaOH eluent, the resolutions between the glucose and fructose also showed good results, similar to the results for Fully (40% Me:6) with the 0.10 mol NaOH eluent.

Table 3: Resolution between glucose and fructose using St-60(40% Me:2, 4, and 6) and fully porous resin (40% Me:6) with 0.10 mol/L NaOH eluent at flow rates of 0.3, 0.5, and 0.7 mL/min.

Flow rate	CH_2-2		CH_2-4		CH_2-6		Fully CH_2-6	
(mL/min)	40%	50%	40%	50%	40%	50%	40%	50%
0.3	1.2	1.8	2.1	1.7	1.7	2.6	3.4	2.9
0.5	1.1	1.6	1.8	1.7	1.5	2.2	3.0	2.6
0.7	1.0	1.5	1.7	1.5	1.4	2.0	3.0	2.3

Theoretical plate numbers (*N*) using St-60(40% Me:2), St-60(40% Me:4), and St-60(40% Me:6) core-shell ion-exchange resins

Resins with different cross-linking degrees in the porous shell (40% and 55%) were further compared in terms of the *N* values of glucose, fructose, and sucrose when using the 0.10 and 0.15 mol/L NaOH eluent at flow rates of 0.3, 0.5, and 0.7 mL/min (Figure 6 (a) and (b)).

Table 4: Resolution between glucose and fructose using St-60(40% Me:2, 4, and 6) and fully porous resin (40% Me:6) with 0.15 mol/L NaOH eluent at a flow rates of 0.3, 0.5, and 0.7 mL/min.
-: Good chromatogram for St-60(40% Me:2) at all flow rates could not be obtained.

Flow rate	CH_2-2		CH_2-4		CH_2-6		Fully CH_2-6	
(mL/min)	40%	50%	40%	50%	40%	50%	40%	50%
0.3	-	1.5	1.8	1.5	2.0	2.1	3.1	2.3
0.5	-	1.3	1.6	1.3	1.7	1.8	2.8	1.9
0.7	-	1.2	1.4	1.2	1.6	1.6	2.6	2.0

Glucose, fructose, and sucrose for St-60(40% Me:2 and 4) showed larger theoretical plate numbers than those of St-60(55% Me:2 and 4) at all flow rates with 0.10 mol/L NaOH eluent. Glucose and fructose for St-60(40% Me:6) and St-60(55% Me:6) showed highly similar theoretical plate numbers at a flow rate of 0.3 mL/min. As the number of methylene groups in the porous shell increased from two to six, the *N* values of glucose and fructose for St-60(40% Me:2, 4, and 6) increased and then decreased at flow rates of 0.3, 0.5, and 0.7 mL/min with 0.10 mol/L NaOH eluent. When the number of methylene groups was four, all carbohydrates showed the largest theoretical plate number at flow rates of 0.3 and 0.5 mL/min.

The theoretical plate numbers of glucose, fructose, and sucrose for Fully (40% Me:6) and Fully (55% Me:6) with 0.10 mol/L NaOH eluent are shown in Figure 6a. When comparing Fully (40% Me:6) and Fully (55% Me:6), glucose for the former showed a smaller theoretical plate number than that of the latter at all flow rates. Fructose for Fully(40% Me:6) showed larger theoretical plate numbers than those of Fully(55% Me:6) at all flow rates.

The theoretical plate numbers of glucose, fructose, and sucrose for Fully (40% Me:6) and Fully (55% Me:6) with 0.15 mol/L NaOH eluent are shown in Figure 6b. Glucose for Fully (40% Me:6) showed smaller theoretical plate numbers than those of Fully (55% Me:6) at all flow rates with 0.15 mol/L NaOH eluent. Fructose for Fully (40% Me:6) had larger theoretical plate numbers than those for Fully (55% Me:6) at all flow rates. *N*-values for fucose exhibited the opposite trend compared with that for glucose.

Mechanism Underlying Retention Time Variation

Table 5 summarizes the glucose retention times and *N* values with the 0.10 mol/L NaOH eluent at a flow rate of 0.5 mL/min, the electrostatic charge on the N^+ atom, and the ion-exchange capacity of the core-shell resins.

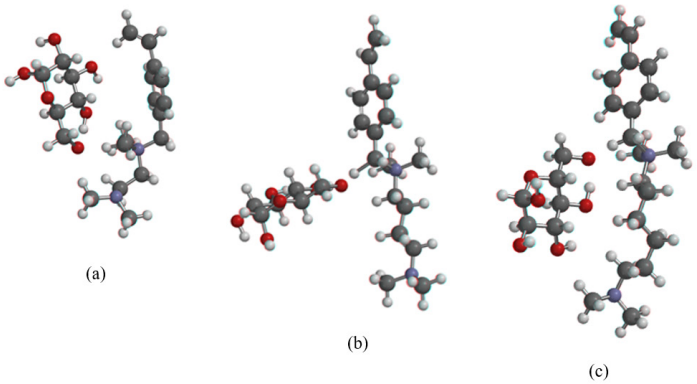
Table 5: Retention time and theoretical plate number *N* of glucose, electrostatic charges on N^+, and ion-exchange capacity of St-60(Me:2), St-60(Me:4), and St-60(Me:6) (Crosslinking 40%, Eluent: 0.10 mol/L and NaOH flow rate: 0.5 mL/min).

Ion-exchange resin	Glu retention time (min)	Theoretical plate number	Electrostatic charge on N^+	Ion-exchange capacity (mEq/mL)
St-60(Me:2)	8.0	4360	+0.720	0.238
St-60(Me:4)	11.8	7200	+0.637	0.378
St-60(Me:6)	12.0	5030	+0.668	0.349

As the number of methylene groups increased from two to six, electrostatic charge decreased initially and then increased, whereas the ion-exchange capacity increased initially and then decreased. Specifically, St-60(40% Me:2) had the largest electrostatic charge and smallest ion-exchange capacity. When increasing the number of methylene groups, electrostatic charge on N^+ decreased and then increased. The retention times of glucose for St-60(40% Me:2, 4, and 6) increased steadily (from 8.0 to 12.0 min) as the number of methylene groups increased.

In our previous study, the ion-exchange capacities of St-60(55% Me:2, 4, and 6) with 0.10 mol/L NaOH eluent increased from 0.294 to 0.360 as the number of methylene groups increased from two to six; however, the retention times of all carbohydrates were approximately the same [35]. We hypothesized that these retention time results could be explained by two opposing factors: the decrease in the positive charge of the N^+ atom in the functional chain and increasing trend in the ion-exchange capacity. For St-60(40% Me: 2, 4, and 6), the positive charge of the N^+ atom in the functional chain decreased and then increased and the ion-exchange capacity increased and then decreased as the number of methylene groups increased.

However, the ion-exchange capacity and glucose retention times of St-60(40% Me: 2, 4, and 6) differed from that of St-60(55% Me: 2, 4, and 6). The stable configuration of these molecules between a monovalent anion of a carbohydrate and cation of an ion-exchange model compound (in Figures 3(a) and (b)) was investigated using Spartan'20 (Figure 7a–c). The distances between the nitrogen N^+ and O^- in complexes were 3.938, 4.206, and 3.187 Å for St-60(40% CH_2:2, 4, and 6), respectively. These results indicate that it is necessary to comprehensively consider many factors to explain differences in carbohydrate retention times.



Figures 7a-c: The most stable configuration of complex between the carbohydrate monovalent negative ion and N+ positive in the porous shell portion for (a) Me:2, (b) Me:4, and (c) Me:6 (calculated using HF 3.21G Spartan' 20).

Discussion

The quantitative determination of carbohydrates can provide valuable information in food chemistry.

In this study, we evaluated the performance of a core-shell ion-exchange resin, St-60(40% Me:2, 4, and 6), with different numbers of methylene groups (two, four, and six) in the functional chains of the polymer in the porous shell. The cross-linking degree was constant at 40%. The carbohydrate separation behavior of a standard solution of inositol, glucose, fructose, and sucrose was used to investigate the HPLC performance of the core-shell ion-exchange resins. Importantly, the sample solution containing carbohydrates can be analyzed using an electrochemical detector without any special pretreatment.

Good chromatograms were achieved for glucose, fructose, and sucrose, regardless of the number of methylene groups. St-60(40% Me:4 and 6) displayed high resolutions (≥1.5) at flow rates of 0.3–0.7 mL/min with 0.10 and 0.15 mol/L NaOH eluent, demonstrating good carbohydrate separation performance. When increasing the number of methylene groups in the functional chain, the retention times of glucose and fructose for St-60 (40% Me:2, 4, and 6) with 0.15 mol/L NaOH eluent increased. St-60(40% Me 2, 4, and 6) at all flow rates with 0.10 and 0.15 mol/L NaOH eluent showed shorter carbohydrate retention times than those for a fully porous resin (40% Me:6) without a dense core. At high pH, carbohydrates become more highly ionized, and their interaction with the porous layer increases. Thus, the elution sequence of the carbohydrates (glucose followed by fructose) was consistent with the pK_a sequence [23]. Various factors contribute the separation properties of the core-shell ion-exchange resins.

First, the core suppresses solute diffusion along the column axis. Because the porous layer is thin, the solute moves across a shorter distance within the shell. The resins evaluated in this study had a size of 5 µm, which is expected to allow effective separation. Second, the concentration of the NaOH eluent plays a critical role in the separation of carbohydrates. Accordingly, optimization of this parameter is expected to allow more effective separation. Finally, St-60(40% Me:4 and 6) with 0.10 and 0.15 mol/L NaOH eluents at all flow rates showed longer retention times for carbohydrates than those of St-60(55% Me:4 and 6).

The increasing trend in retention times as the number of methylene groups increased may not be explained by the electrostatic charge on the N^+ atom in the functional chain. Based on this result, other factors should be considered to explain the differences in carbohydrate retention times. It is necessary to determine the separation conditions for ion-exchange resins that provide the shortest retention time for sucrose and high resolution.

The resins with a short sucrose retention time of 17 min or less and resolution of ≥1.5 under 0.10 ml/L were as follows: St-60(40% Me:4 and 6) at flow rate of 0.5 mL/min and St-60(40% Me:4) at flow rate of 0.7 mL/min. The resins with a short sucrose retention time of 17 min or less and resolution of ≥1.5 under conditions of 0.15 mol/L were as follows: St-60(40% Me:4 and 6) at a flow rate of 0.5 mL/min and St-60(40% Me:4) at flow rate of 0.7 mL/min. The performance of resins could not be fully explained by the four factors evaluated in this study (concentration of the NaOH eluent, thickness of the shell portion, electrostatic charge on the N^+ atom, and ion-exchange capacity). Thus, a wider range of parameters should be evaluated.

For example, the stabilization energy between the negative ion and N^+ of functional groups of carbohydrates may play a crucial role in molecular interactions. This perspective should be considered when designing further experiments. Our data on this complex obtained through Spartan may serve as basis for future research.

Conclusions

Analyses of retention time resolution and theoretical plate number under various numbers of methyl groups suggested that St-60(40% Me 2, 4, and 6) core-shell ion-exchange resins are highly efficient for carbohydrate analyses, e.g., with respect to the retention time and resolution between glucose and fructose. Their suitability for strongly alkaline conditions allows their effective use in electrochemical detection. These resins also possess outstanding durability owing to their polymeric core and shell.

Abbreviations

St-60(40% Me:2, Me:4, and Me:6): constant core-shell monomer weight ratio of 40:60, degree of cross-linking of 40%, with two, four, and six methylene groups in the porous layer, respectively.
Rt: Retention time
N: Theoretical plate number.

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