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Exploration of deep eutectic solvent-based mesoporous silica spheres as high-performance size exclusion chromatography packing materials

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ABSTRACT: Choline chloride (ChCl) with three alcohol-based deep eutectic solvents (DESs) was applied as a new type of green solvent for the modification of mesoporous silica spheres. The mesoporous silica spheres were characterized by field emission scanning electron microscopy and Brunauer–Emmett–Teller surface area analysis. Many uniform and mesoporous silica spheres were obtained with a ChCl–1,2-butanediol DES as a reactant. The DES-modified mesoporous silica spheres were used for the adsorption of polysaccharides (alginic acid, fucoidan, and laminarin). The adsorption results show that the ChCl–1,2-butanediol DES-based silica spheres had stable interactions with the target compounds. A comparison of the three sorbents as size exclusion chromatography packing materials showed that the ChCl–1,2-butanediol DES-based silica spheres produced good resolution of the three test polysaccharides and exhibited the best separation capability. This was attributed to the uniform mesoporous structure of the ChCl–1,2-butanediol DES-based silica spheres. Therefore, more DESs should be applied to the preparation of mesoporous silica spheres in future studies.
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INTRODUCTION

In recent years, ecofriendly solvents have attracted considerable interest and are used widely in areas such as electrochemistry, biochemistry, inorganic chemistry, organic chemistry, analytical chemistry, and physical chemistry.[1,2] Among these ecofriendly solvents, ionic liquids (ILs) have been studied extensively since the 1970s.[3] In some studies, ILs have shown green properties but also toxicity and poor biodegradability; this has hindered their further development.[4,5] To overcome the disadvantages of ILs, deep eutectic solvents (DESs), a new type of ecofriendly solvent, have attracted considerable interest since their first description by Abbot *et al.* in 2003.[6]

According to Abbot *et al.*, a DES is composed of quaternary ammonium salts with hydrogen donors forming a eutectic with a much lower melting point than either of the individual components.[6] Since the appearance of the DES definition, these compounds have been applied widely in the synthesis, electrodeposition, and preparation of nanomaterials; the separation of biodiesel; and many chemistry fields.[7] On the other hand, DESs, as a type of ecofriendly solvent, have never been applied to the conventional hydrothermal synthesis of mesoporous silica spheres. The structural adjustability of DESs can be developed for the preparation of mesoporous silica spheres. Therefore, in this study, DESs were first applied to the preparation of mesoporous silica spheres. In addition, mesoporous siliceous particles with uniform pore structures and excellent stability were applied as packing materials for high-performance size exclusion chromatography (HP-SEC).[8,9] Normally, HP-SEC with a single column containing microscale packing materials can be operated easily on an HP-SEC system and can be applied to the separation and analysis of large molecules.[10] Accordingly, DES-based mesoporous silica spheres were evaluated as HP-SEC packing materials.

In this study, the preparation of DES-based mesoporous silica spheres was explored, and DES-based mesoporous silica spheres were characterized with related analysis techniques. Polysaccharides are popular large molecules with properties suitable for biotechnological, pharmaceutical, and medical applications.[11] Therefore, DES-based mesoporous silica spheres as HP-SEC packing materials were evaluated with three polysaccharides: alginic acid, fucoidan, and laminarin.

EXPERIMENTAL

Materials

Ammonium fluoride (NH_4F; 98%), poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEG–PPG–PEG), and the standard chemicals of polysaccharides were obtained from Sigma-Aldrich (St. Louis, MO). Ethylene glycol

Table I. NH_4F-Based DESs

Abbreviation	Salt	HBD	Salt/HBD molar ratio
DES-1	H_4NF (45 mg)	Glycerol (112 mg)	1 : 1
DES-2		Ethyl glycol (75 mg)	
DES-3		1,2-Butanediol (109 mg)	

(>99.5%), glycerol (>99.0%), 1,2-butanediol (>98.0%), and 1,3,5-trimethylbenzene (TMB; 99%) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Tetraethoxysilane (TEOS; 98%) was supplied by Alfa Aesar (Heysham, England). Hydrochloric acid (HCl; 36%) was acquired from Kosdaq Co., Ltd. (Siheung, Korean). All other organic solvents and inorganic reagents were supplied by Duksan Pure Chemicals Co., Ltd. (Ansan, Korea). Distilled water was filtered with a vacuum pump and filter (HA-0.45, both from Millipore) before use.

Preparation and Characterization of the DES-Based Mesoporous Silica Spheres

First, the DESs were prepared by the heating of NH_4F and the hydrogen donor mixtures at a molar ratio of 1 : 1 at 100°C with constant stirring until a homogeneous liquid formed (Table I). Second, DES-based mesoporous silica spheres were prepared with a hydrothermal polymerization method according to a methodology reported elsewhere.[12–14] The DES-based mesoporous silica spheres were synthesized with the following synthetic scheme. An amount of 4.0 g of PEG–PPG–PEG as a copolymer was dissolved in 65.0 mL of H_2O and 10.0 mL of HCl solution in a reactor; this was followed by the addition of 5.0 g of TMB. The mixture was stirred at 40°C for 2 h. Subsequently, 9.0 mL of TEOS was added to the reaction mixture, and the mixture was transferred to an autoclave at 40°C for 20 h. The DES was then added to the autoclave, and the temperature was increased to 150°C and held at that temperature for 24 h. After aging, the resulting white precipitate was filtered, washed sequentially with water and ethanol, and dried at 60°C. The resulting white powder was then calcined at 900°C in a muffle furnace for 6 h. After cooling, the desired DES-based mesoporous silica spheres were obtained as white particles.

The DES-based mesoporous silica spheres were characterized by field emission scanning electron microscopy (S-4200, Hitachi, Ontario, Canada) and Brunauer–Emmett–Teller (BET) surface area analysis.[15] The BET surface area (N_2 atmosphere at −195.8°C) was measured with an ASAP2020 surface area analyzer (Micromeritics, Norcross, GA).

Adsorption on the DES-Based Mesoporous Silica Spheres

We tested the adsorption properties of the DES-based mesoporous silica spheres by shaking the material with 1.0 mL of a polysaccharide solution. After adsorption of the polysaccharide to the DES-modified silica, the change in the polysaccharide concentration in solution was analyzed by commercial HP-SEC.

The HP-SEC system consisted of an M930 solvent delivery pump (Younglin, Korea) and a refractive-index detector (Younglin, Korea). HP-SEC was performed with a Waters Ultrahydrogel WATO 11530 size exclusion column (300 × 7.8 mm *i.d.*) and a Waters Ultrahydrogel WATO 11565 guard column (40 × 6 mm *i.d.*) from Waters (Milford, MA). To prepare the calibration curve, a series of accurate concentrations (0.01, 0.05, 0.1, 1.0, and 5.0 mg/mL, respectively) of aqueous alginic acid, fucoidan, and laminarin solutions were obtained, and 5.0 μL of each standard solution was injected. The column was eluted with water as the mobile phase at 40°C at a flow rate of 1.0 mL/min.

The quantity of the target compounds adsorbed on all of the sorbents in the equilibrium results were calculated with the following equation:

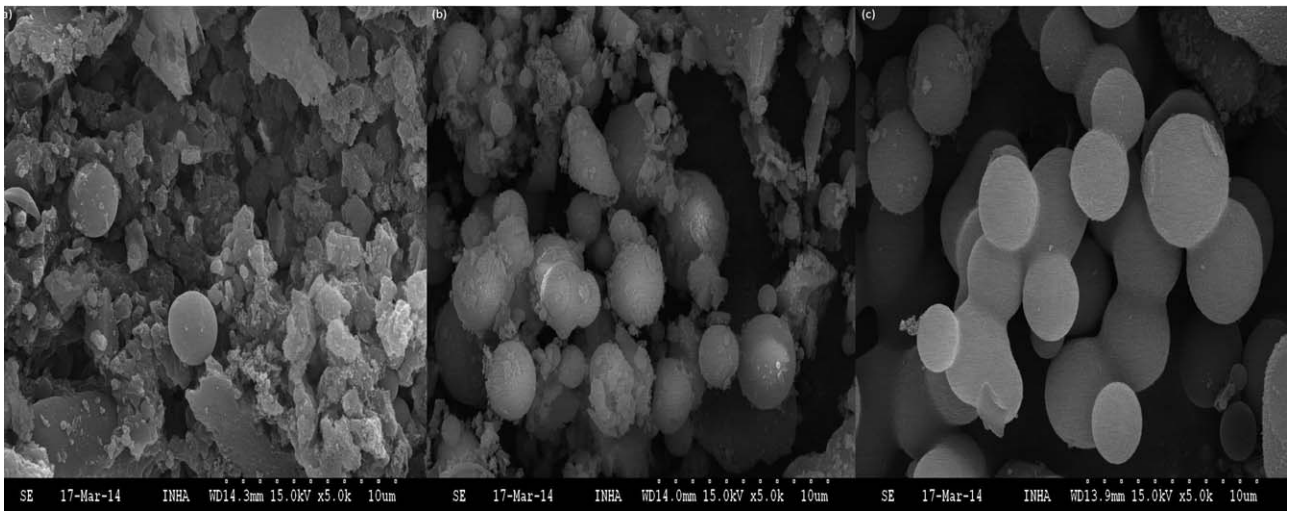

Figure 1. Low-magnification scanning electron microscopy images of the mesoporous silica spheres based on (a) DES-1, (b) DES-2, and (c) DES-3.

Table II. BET Data for the DES-Based Silica Spheres

Silica sphere	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
DES-1-based	45.6	0.28	241.7
DES-2-based	25.3	0.08	131.5
DES-3-based	175.5	0.68	155.1

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where Q_e is the amount adsorbed at equilibrium (mg/g), C_0 (mg/mL) is the initial concentration of the target compound, C_e (mg/mL) is the unadsorbed concentration at equilibrium, V is the volume of solution (mL), and m is the mass of the adsorbent (g).

The Langmuir isotherm, Freundlich isotherm, and Temkin isotherm are normally used to determine the equilibrium characteristics of adsorption.

The Langmuir equation can be expressed as follows:

$$\frac{C_e}{Q_e} = aC_e + b \quad (2)$$

The Freundlich isotherm can be written as follows

$$\log Q_e = c \log C_e + d \quad (3)$$

The Temkin isotherm is given by the following equation:

$$Q_e = e \ln C_e + f \quad (4)$$

The numerical coefficient a, b, c, d, e and f in competitive Langmuir, Freundlich, and Temkin isotherm models were derived from the experimental values of the retention factors, respectively.

Testing of the DES-Based Mesoporous Silica Spheres as Packing Materials

The DES-based mesoporous silica spheres were packed in a 250 × 4.6 mm stainless steel column with a wet-packing method. The packing materials were first dispersed in ethanol, and the slurry was packed under a pressure of 40 MPa. A mixture solution of alginic acid, fucoidan, and laminarin was selected as the evaluated compound. These homemade columns were used under the same conditions as used for the previous commercial column.

RESULTS AND DISCUSSION

Characterization of the DES-Based Mesoporous Silica Spheres

In previous studies, the mesoporous silica sphere structure was affected by each reagent in synthesis, such as the copolymer of PEG-PPG–PEG, TEOS, HCl, TMB, and inorganic salts.[16,17] A DES is composed of a salt with a hydrogen donor; the DES not only experiences hydrophobic and π–π interactions with the copolymer but also hydrogen-bonding interactions with the —OH groups of the copolymer. In addition, DES is an eco-friendly solvent. In this study, we examined the use of DES instead of a single salt in the preparation of mesoporous silica spheres while fixing the polymer, TEOS, HCl concentrations, and TMB. Three NH_4F-based DESs were selected for the synthesis of mesoporous silica spheres, as shown in Table I.

A significant difference in the shapes of the mesoporous-silica-sphere-based DESs was observed, as shown in Figure 1. Scanning electron microscopy revealed only a few spheres in the prepared materials based on DES-1 [Figure 1(a)], and

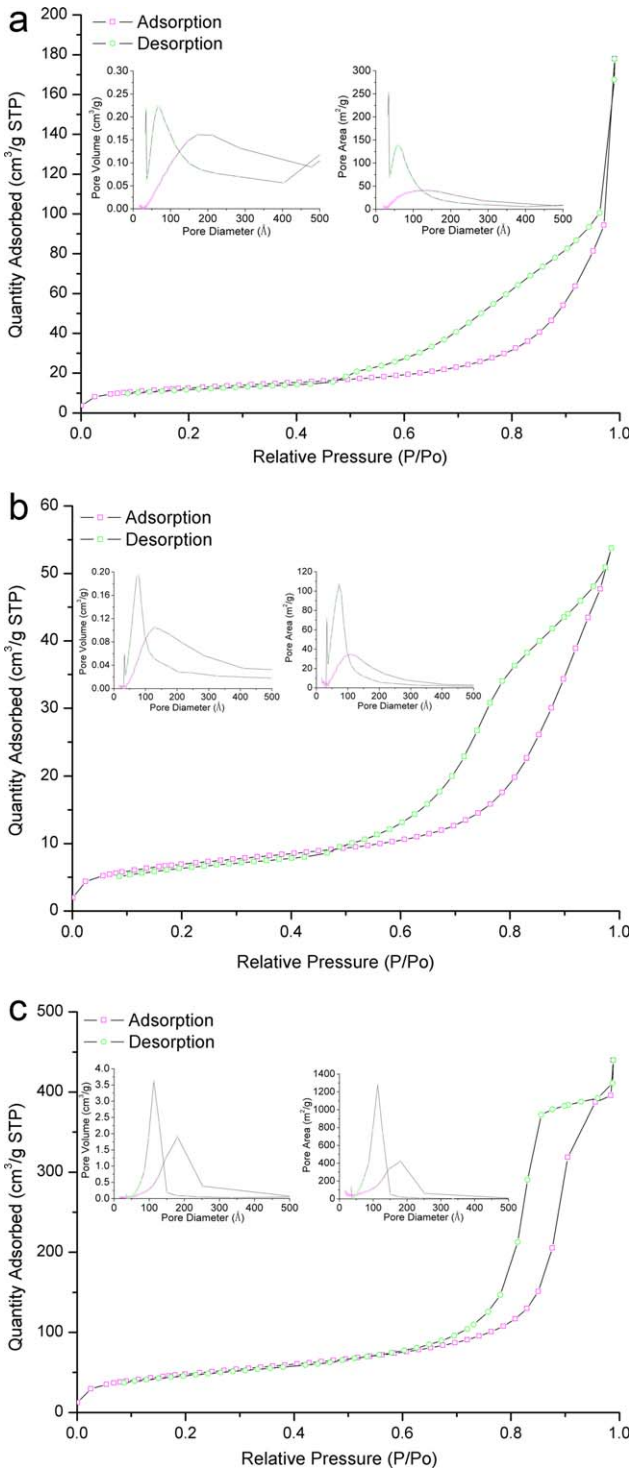

Figure 2. Isotherm, pore volume distribution, and pore area distribution of the mesoporous silica spheres based on (a) DES-1, (b) DES-1, and (c) DES-1 in the nitrogen adsorption–desorption process. P_0 = atmospheric pressure; P = pressure change. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

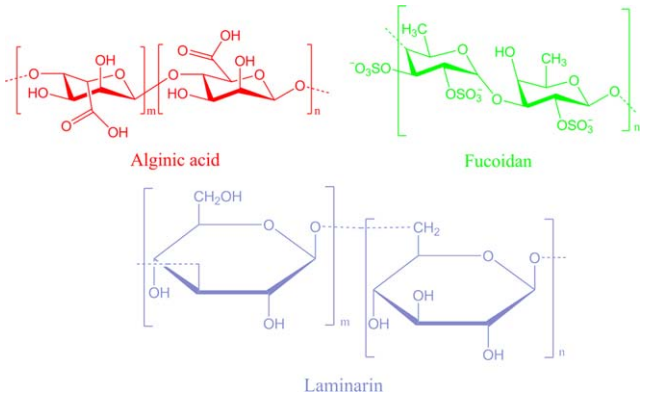

Figure 3. Molecular structures of the three macromolecules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

although there were more spheres based on DES-2 than on DES-1, there were many irregular materials attached to the surface of the silica-sphere-based DES-2 [Figure 1(b)]. On the other hand, many smooth-faced silica spheres based on DES-3 were formed [Figure 1(c)]. The three DESs had different hydrogen donors in each DES (Table I). Therefore, the hydrogen donor in the DESs might have affected the mesoporous materials formed. DES-1, with glycerol containing three hydroxyl groups as the hydrogen donor, exhibited hygroscopic behavior but did not interact easily with the other inorganic regents, so few silica spheres were obtained. DES-2, with ethyl glycol containing two hydroxyl groups, interacted more easily with the other regents than DES-1, and more silica spheres were obtained. DES-3, with 1,2-butanediol containing two hydroxyl groups and a four-carbon chain, exhibited hydrophobicity and interacted more easily with the other inorganic regents than DES-2. Therefore, many uniform silica spheres were formed with DES-3.

Table II and Figure 2(a–c) show the structural parameters of the mesoporous silica spheres from the BET data. The mesoporous-silica-sphere-based DES-3 showed the largest surface area and the largest pore volume among the three materials. The surface and pore volume of the DES-1-based material or DES-2-based material were less than those of the DES-3-based material. The irregular shapes of the DES-1-based material may have result in the largest pore size with the DES-1-based material. The hysteresis of the N_2 adsorption and desorption isotherms of the mesoporous-sphere-based DES-3 [Figure 2(c)] was significantly more regular than the those of the DES-1-based materials [Figure 2(a)] and DES-2-based materials [Figure 2(b)]. Similarly, the pore volume distribution and pore area distribution of the mesoporous-sphere-based DES-3 was relatively symmetrical, but those of the distribution-based DES-1 and DES-2 were asymmetric. In fact, the BET data were consistent with the scanning electron microscopy images shown in Figure 1.

Adsorption Properties of the DES-Based Mesoporous Silica Spheres

Adsorption Equilibrium. The adsorption equilibrium data is a basic requirement for the design of adsorbents for the separation of target compounds.[18] Therefore, in this study, three polysaccharides were selected as adsorbates for evaluation of the three adsorbents (Figure 3). The adsorption equilibrium is also an important analysis factor for design purposes.

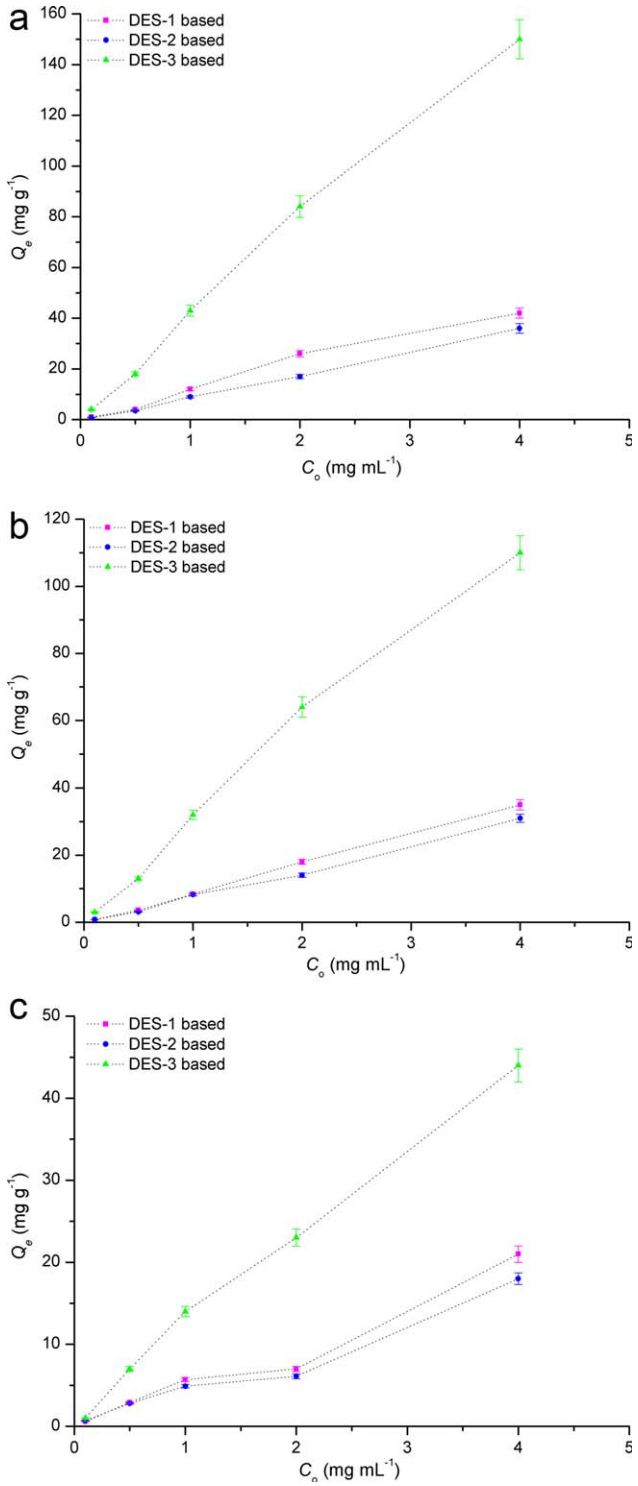

Figure 4. Amounts of (a) alginic acid, (b) fucoidan, and (c) laminarin adsorbed onto the three DES-modified silica spheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Data for the Three DES-Based Silica Spheres Fitted with Three Adsorption Equations

		Langmuir equation			Freundlich equation			Temkin equation		
Target compound	Silica sphere	*a*	*b*	R^2	*c*	*d*	R^2	*e*	*f*	R^2
Alginic acid	DES-1-based	−0.004	20.310	0.110	1.061	−1.062	0.984	10.870	−1.879	0.809
	DES-2-based	−0.005	23.974	0.243	1.039	−0.933	0.994	8.670	−1.821	0.755
	DES-3-based	0.001	−10.797	0.925	0.929	−1.966	0.991	25.288	−3.328	0.679
Fucoidan	DES-1-based	−0.004	27.616	0.370	1.028	−0.935	0.997	8.440	−1.838	0.759
	DES-2-based	−0.001	95.455	0.013	0.986	−0.920	0.992	7.277	−1.846	0.742
	DES-3-based	−0.001	216.468	0.918	0.995	−1.645	0.992	27.635	−2.182	0.618
Laminarin	DES-1-based	0.012	−13.976	0.124	4.597	−1.870	0.677	0.907	−0.807	0.978
	DES-2-based	0.025	−6.819	0.261	3.837	−1.942	0.672	0.812	−0.852	0.973
	DES-3-based	0.003	−27.210	0.890	10.730	−1.993	0.831	1.011	−1.134	0.689

Figure 4 shows the amount of polysaccharides adsorbed on the mesoporous-sphere-based DESs. The Q_e values of the three adsorbents at the C_0 values of three polysaccharides (0.1, 0.5, 1.0, 2.0, and 4.0 mg/mL) were examined according to the equilibrium time. The Q_e value for each adsorbent increased with increasing initial acid concentration from 0.1 to 4.0 mg/mL. In this result, C_0 provided an important driving force for the mass transfer of the target compounds from the adsorbate to the adsorbents, and a higher C_0 of adsorbate increased the rate of mass transfer.[19] In addition, the order of Q_e of each polysaccharide at the same C_0 on the three mesoporous spheres were as follows: DES-3-based > DES-1-based >DES-2-based. On the basis of the porous structure of all of the sorbents characterized by the BET surface area data, even the DES-1-based materials with a few spheres could adsorb more of the target compounds than the DES-2-based materials. On the other hand, the uniform surface areas, pore sizes, and the functional groups of the DES-3-based porous silica spheres adsorbed the largest quantity of the target compounds. In addition, the surface area of the DES-3-based sorbent was the largest among the three sorbents, and the strength of the interaction between the DES functional groups and the target compounds affected the amount adsorbed.

Adsorption Isotherms. Three line isotherms of Langmuir, Freundlich, and Temkin were selected to evaluate the equilibrium characteristics of adsorption between the adsorbate and adsorbent and to help select a suitable adsorbent for the packing column in HP-SEC. Although the three isotherms had more than one form of related equations,[20] three linear equations for the three isotherms were selected. R^2 is coefficient of determination. The *a*, *b*, *c*, *d*, *e*, *f*, and R^2 values were calculated from the relatively straight lines according to the previous three equation, as shown in Table III. According to the regression coefficient in Table III, the Langmuir and Freundlich equations fixed with the DES-3-based sorbent were evidently better than the other two sorbents, but the Temkin equation fixing the DES-1 or DES-2-based sorbents was better than the DES-3-based sorbent. The uniform DES-3-based sorbents had a good adsorption effect on the target compounds; this means that the DES-3-based sorbent underwent a stable interaction with the target compounds and is a possible sorbent for a size exclusion chromatography (SEC) columns.

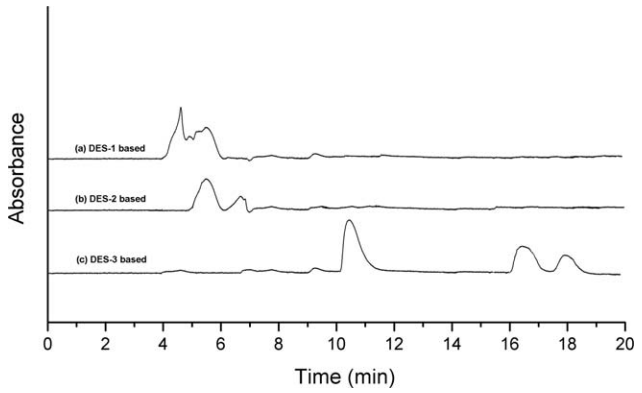

Figure 5. Separation of the alginic acid, fucoidan, and laminarin standards by the three HP-SEC columns: (a) DES-1-based, (b) DES-2-based, and (c) DES-3-based.

Application of DES-Based Mesoporous Silica Spheres in HP-SEC

To validate the DES-based sorbents as SEC packing materials, the previous three polysaccharides were also selected as target compounds to evaluate the properties of their packing columns. Figure 5 presents the separation results of the three target compounds by three DES-based HP-SEC experiments. In addition, the resolution of the three targets compounds was not obtained clearly by the DES-1- or DES-2-based SEC columns, but a high resolution was obtained with the DES-3-based SEC column. Figure 5(a,b) shows that the uneven DES-1- or DES-2-based sorbents was unsuitable for forming the interparticulate voids from the packing particles, and the related SEC column did not have a good resolution for the solutes. The uniform DES-2-based mesoporous particles, however, formed uniform interparticulate voids in the SEC packing column and showed good separation of the target compounds.

CONCLUSIONS

DES, an ecofriendly solvent, was first applied to modify mesoporous silica spheres with a slight modification of a conventional hydrothermal synthesis method. In this study, the DES-3-based mesoporous silica spheres possessed better adsorption properties than the other two adsorbents. In addition, the DES-

3-based sorbents as packing materials also showed better resolution for the three polysaccharides. Overall, the DES-based sorbents were viable alternative packing materials for SEC columns.

ACKNOWLEDGMENTS

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