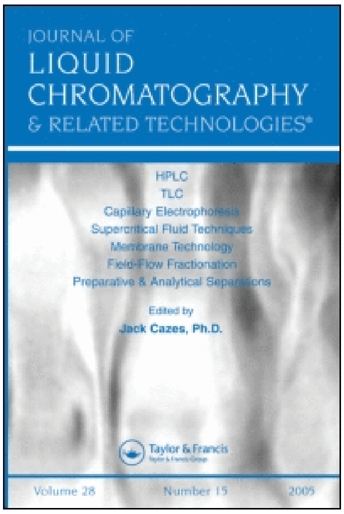

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Adsorption of Synthetic Water-Soluble Polymers from Thermodynamically Good Solvents onto Microporous Column Packings

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ABSTRACT

The elution behavior of polyethylene glycols, polyethylene oxide, polypropylene glycols, and sodium poly(methacrylic acid) in several mobile phases (water, methanol, acetone, dimethylacetamide, diethylene glycol monobutyl ether) was studied. The elution behavior of polyvinyl alcohol in water was also measured. ZSM-5 and Y-type zeolites were used as column packings. Full retention of the polymers was found in several chromatographic systems. Polyethylene oxide with average molar masses up to 545 kg/mol, polyvinyl alcohol up to 128 kg/mol, and sodium poly (methacrylic acid) up to 1027 kg/mol were fully retained within specific

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column packings. Additionally, to the full adsorption, a decreased recovery of polymers was observed in some sorbent–solvent systems. According to the hydrodynamic radius of macromolecules in solution, the polymer should be sterically fully excluded from all pores of the zeolites. It is assumed that polymer chains are adsorbed in flower-like conformation, i.e., a part of polymer chain could penetrate into pores after a change in the conformation of chains. The results indicate that microporous sorbents possess high adsorption potential towards polymers.

Key Words: Adsorption; Water-soluble polymers; Microporous column packings; Zeolites.

INTRODUCTION

Zeolites are porous materials with pores formed by free open channels, or cages, inside their crystal structures. The crystal structure consists of SiO_4 and AlO_4 tetrahedra. As a consequence, the pores have precisely defined geometrical dimensions and space distribution.[1] The pore dimensions in the zeolite crystals correlate with the dimensions of molecules. As a consequence, the adsorption on zeolites may be very selective with regard to the shape of the molecules. Zeolites are well known as sorbents and catalysts.[1,2] They are used for adsorption and separation of molecules in gas phase systems and in liquids. For example, adsorption of alkanes from various organic liquids to zeolites has been described,[3–8] adsorption of saccharides or alcohols from water to zeolites was reported,[9–16] and adsorption of amino acids from water was described.[17]

Recently, it was observed that a non-polar polymer, polyethylene, with the molar masses as high as 500 kg/mol was fully retained from decalin within a HPLC column packed with a ZSM-5 type zeolite.[18] Thus, microporous zeolites are the first sorbents where strong retention of polyethylene was observed. The fact that polyethylene chains can be adsorbed by the zeolite, encouraged us to extend our chromatographic investigations to some polar water-soluble polymers.

The chromatographic behavior and adsorption of polyethylene oxide (PEO), polyethylene glycol (PEG), or polypropylene glycol (PPG) was studied by many authors in various sorbent–solvent systems.[19–28] According to our knowledge, however, interactions between zeolites and synthetic polymers were studied experimentally only by Buttersack et al.[14] and Chang et al.[29] Buttersack et al.[14] have determined adsorption equilibrium constants under static conditions. It was shown that dextran and PEO were adsorbed from the aqueous phase on a FAU-type zeolite. The highest investigated molar mass of dextran and PEO was 40 kg/mol. Also, sodium polyacrylate with a weight-average molar mass of 6 kg/mol was adsorbed on the same zeolite from water at pH 2.5.[14] Chang et al.[29] have measured adsorption of PEG 6 kg/mol in water onto a DAY-type zeolite. Adsorption isotherms and adsorption kinetics were evaluated.

The attractive interactions between polymers and zeolites are of interest from the point of HPLC separation of synthetic polymers. In this paper, a series of chromatographic measurements with water-soluble polymers and zeolite column packings is described.

EXPERIMENTAL

Sorbents

Four HPLC columns were prepared by manually packing zeolite crystals into stainless steel columns with an internal diameter of 4.6 mm.

The first 150 mm column contained silicalite (Alsi-Penta Zeolithe GmbH, Schwandorf, Germany), with a Si/Al ratio of 400. The pore system of silicalite contains linear channels with free pore diameters of 5.6 × 5.3 Å, intersecting with sinusoidal channels, having a free diameter of 5.5 × 5.1 Å. This material has a particle size larger than 10 μm.

The second column, with a length 150 mm, contained zeolite SH-300 (Alsi-Penta product), a ZSM-5 material with a Si/Al ratio of 150. SH-300 has an identical pore system as silicalite and an average particle size of about 10 μm.

The third column with a length of 50 mm was filled with an ultrastable Y zeolite, USY CBV-780 (Zeolyst Int., Valley Forge, PA), with a Si/Al ratio of 40. This zeolite contains free cavities with a diameter of 12 Å. These cavities are connected through windows with a size of 7.3 Å. This zeolite also contains larger mesopores, with a size between 40 and 400 Å.[30] The CBV-780 crystals have an irregular spherical morphology, with an average particle size of 0.5 μm.

The fourth column, with a length of 50 mm, was packed with zeolite CP 814E H-Beta (Zeolyst product), with a Si/Al ratio of 12.5. The channel system of the zeolite CP 814E H-Beta constitutes of three interconnecting pore systems. Two 12-ring linear channels (5.7 × 7.5 Å) in different crystallographic directions intersect partially. A third, sinusoidal channel (5.6 × 6.5 Å) is formed by these intersections. These cavities have a diameter of 7.6 Å. The average particle size is about 1 μm.

The sorption properties of the used column packing materials were described by Denayer et al.[8] Generally, the higher the Si/Al ratio of a zeolite is, the more hydrophobic it behaves.

Polymers

Sodium poly(methacrylic acid) (weight average molar mass 1.25; 31.5; 143; and 1027 kg/mol), polypropylene glycols (PPG, 0.435; 1; and 3 kg/mol), and polyvinyl alcohols (PVA, 8.81; 29.6; 78.9; and 128.5 kg/mol) were obtained from Polymer Standards Service, Mainz, Germany. Polyethylene oxide samples (PEO, 27.25; 83.8; 253; 545 kg/mol) and polyethylene glycol (PEG, 1.5; 6; 35 kg/mol) were delivered by Polymer Laboratories, Church Stretton, England.

Mobile Phases

Water, methanol, acetone, dimethylacetamide (DMAC), diethylene glycol monobutyl ether (DEGMBE), all of synthesis quality (Merck, Darmstadt, Germany), were used in this study. Water with a $pH = 3$ was prepared by addition of 3 mL of acetic acid p.a. (Jansen Chimica, Geel, Belgium) into 1 L deionized water. Water with $pH = 10$ was prepared by mixing 12 mL ammonium hydroxide (25% solution, Merck, Darmstadt, Germany) with 1 L deionized water.

HPLC Assembly

An Agilent 1100 Series chromatograph (Agilent Technologies, Inc., Waldbronn, Germany) was connected with an evaporative light scattering detector (ELSD), model PL-ELS 1000 (Polymer Laboratories, Church Stretton, England). The parameters of the ELSD recommended in the manual by the producer for the used liquids were used. The temperature of the column oven was maintained at 30°C. Polymer solutions (50 μL) and 100 μL were injected. The polymer concentration was around 1 mg/mL. The flow rate of the mobile phase was in the range 0.4–1 mL/min, depending on pressure resistance of a tested column.

For some measurements, a Waters 150C chromatograph was used with the same operational parameters as described above. For DEGMBE, however, the temperature of injector and column measurements was set at 65°C.

Determination of Critical Diameters

Working with zeolites, it is assumed that only molecules with a diameter (so called critical diameter), which is smaller than the zeolite pore size, may enter into the pore volume. The critical diameter of a molecule is the diameter of the smallest cylinder that can circumscribe the molecule.[5] We have constructed models of molecules and macromolecules by computer simulations using the software "Materials Studio" (Accelrys Inc., San Diego). The computer simulations were done with force field methods using the COMPASS force field. When constructing the molecules by the software, bond angles, bond lengths, and van der Waals radii of atoms were respected. Influences of both temperature and pressure on the bond lengths and radii were neglected. In the case of the polymer chain, a prolonged conformation of the chain was considered. Critical diameters were estimated for an equilibrium conformation of a molecule. Influence of interactions between zeolite and molecule on the critical diameter was not considered.

RESULTS AND DISCUSSION

The series of polyethylene glycol, polyethylene oxide, polypropylene glycol, and sodium poly(methacrylic acid) samples were injected into four columns using several mobile phases. A summary of their elution behavior is shown in Table 1.

The chromatographic behavior of the polymers tested depended on the column packing used. When zeolite SH-300 or CBV-780 was selected, polyethylene oxide and polyethylene glycols were fully retained from the majority of the tested mobile phases (Table 1). No peaks were detected on the chromatograms in these cases. In a few cases, very small peaks of polymers were detected (Fig. 1).

The comparison of peak areas obtained under identical conditions, with the column and without the column, enables evaluation of the recovery of the injected polymer samples. For example, the difference between peak areas obtained without and with the column in Fig. 2 illustrates partial elution of polypropylene glycols from zeolite CP814E. The recovery of polymer samples from the column, i.e., the height or area of polymer peaks (Fig. 2), increases with their molar masses. This indicates that shorter chains are retained to a larger extent than longer chains. This effect was also observed for polyethylene samples and identical zeolites as used in this work.[18] Shorter chains may diffuse into the pores easier, and thus, their retention is larger. Moreover, macromolecules with smaller molar masses may change their conformations more easily, a prerequisite for their penetration into the narrow pores of the zeolites.

PEG, PEO in both acetone and in DEGMBE: PPG and sodium poly(methacrylic acid) in water eluted from the columns, while the height of the polymer peaks decreased with increasing molar masses. This effect was also found, however, when measuring the polymer samples without the columns (see chromatograms in Fig. 1 or Fig. 3, without column). It means

Table 1. Elution behavior of polymers.

Sorbent	Mobile phase	PEG	PEO	PPG	PVA	Sodium poly(methacrylic acid)
Silicalite	Water	Eluted	Eluted	Eluted[a]	Eluted	Eluted
Si/Al = 400	Methanol	Eluted	Eluted	Eluted		Not soluble[b]
pores 5–6 Å	Acetone	Almost fully retained	Almost fully retained	Eluted		
	Water, pH = 3	Fully retained	Fully retained	Eluted[a]		Eluted
	Water, pH = 10	Eluted	Eluted	Eluted[a]		Eluted
	DMAC	Eluted	Eluted	Eluted		Not soluble[b]
	DEGMBE	Eluted	Eluted	Eluted		
SH-300	Water	Fully retained	Fully retained	Eluted[a]	Fully retained	Eluted
Si/Al = 150	Methanol	Fully retained	Partially retained	Eluted		Not soluble[b]
pores 5–6 Å						
	Acetone	Fully retained	Fully retained	Eluted		
	Water, pH = 3	Fully retained	Fully retained	Eluted[a]		Eluted
	Water, pH = 10	Fully retained	Fully retained	Eluted[a]		Eluted
	DMAC	Eluted	Eluted	Eluted		Not soluble[b]

CBV-780 Si/Al = 40 pores 7–12 Å mesopores 40–400 Å	Water	Fully retained	Fully retained	Fully retained[a]	Fully retained	Almost fully retained
	Methanol	Fully retained	Fully retained	Fully retained		Not soluble[b]
	Acetone	Fully retained	Fully retained	Fully retained		
	Water, pH = 3	Fully retained	Fully retained	Fully retained[a]		Partially retained
	Water, pH = 10	High pressure resistance of the column packing				
	DMAC	Eluted	Eluted	Eluted		Not soluble[b]
CP 814E Beta Si/Al = 12.5 pores 5.7 × 7.5 Å; 5.6 × 6.5 Å	Water	Partially retained	Partially retained	Eluted[a]	Fully retained	Almost fully retained
	Methanol	Fully retained	Fully retained	Fully retained		Not soluble[b]
	Acetone	Fully retained	Fully retained	Partially retained		
	Water, pH = 3	Fully retained	Fully retained	Fully retained[a]		Fully retained
	Water, pH = 10	High pressure resistance of the column packing				
	DMAC	Eluted	Eluted	Eluted		Not soluble[b]

[a] PPG 3 kDa only partially soluble.

[b] Polymer samples were not soluble in the mobile phase.

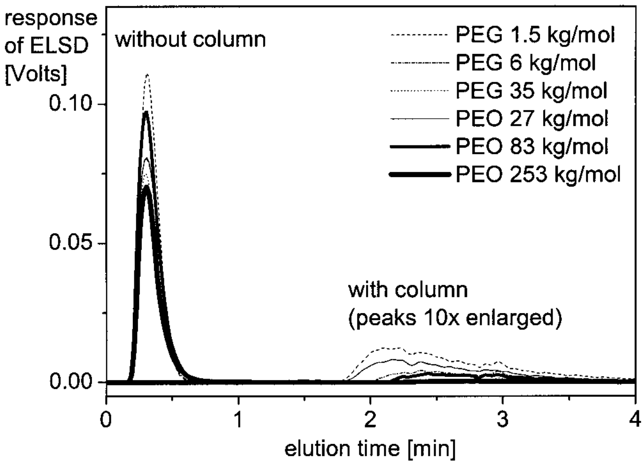

Figure 1. Chromatograms of polyethylene glycol and polyethylene oxide samples obtained without and with column. Column packing: silicalite. Mobile phase: acetone.

that the response of the ELSD depends in some solvents pronouncedly on the molar mass of the samples. The concentrations of the polymers were similar, as well as the peak areas without the column and with the column, which indicates that the polymers were not retained in the column packing. In this case, the ELSD response decreased with increasing molar masses, which

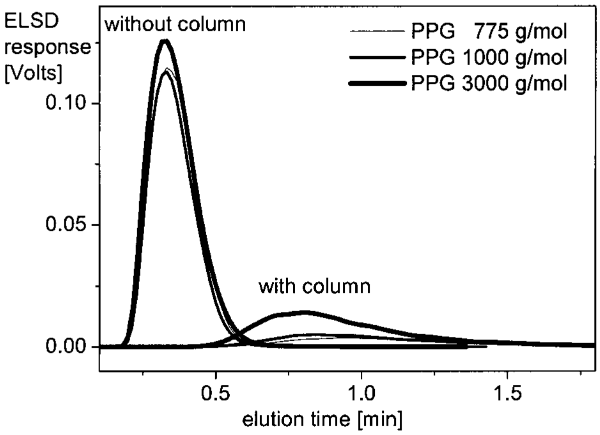

Figure 2. Chromatograms of polypropylene glycol samples obtained without and with column. Column packing: zeolite CP814E. Mobile phase: acetone.

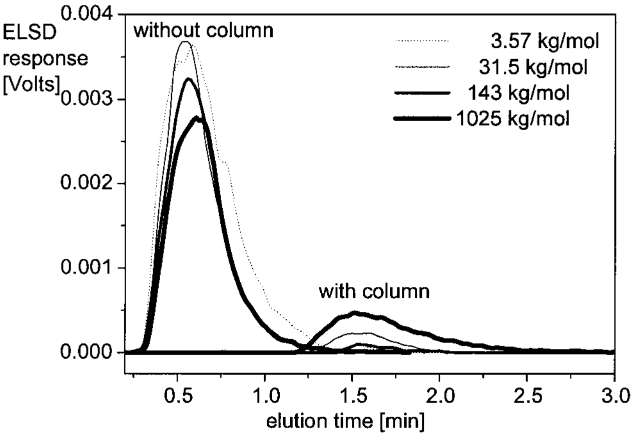

Figure 3. Chromatograms of sodium poly(methacrylic acid) samples obtained without and with column. Column packing: zeolite CBV-780. Mobile phase: water, pH = 3.

was not observed in other tested systems. The formation of droplets, which are detected in the ELSD depends on a series of parameters. Also, at constant gas and flow rate of the mobile phase and the nebulization temperature, the surface tension of the eluent, density, viscosity, and the formation of molecular aggregates of solutes with solvent molecules play a decisive role.[31]

A comparison of the elution behavior of PEG and PPG shows the influence of the pore size of the zeolites on chromatographic behavior. While PEG is fully retained from some solvents in a column packed with SH-300 and silicalite, PPG is fully eluted from silicalite and zeolite SH-300 (Table 1). The pores in SH-300 are too small for chains containing many methyl branches.[18] Using a zeolite with larger pore size (CBV-780, CP814E, Table 1), PPG is fully or partially retained within the column. The same is valid for sodium poly(methacrylic acid) standards.

Sodium poly(methacrylic acid) samples were fully retained from water in both CBV-780 and CP814E column packings. According to Buttersack et al.,[14] a change in pH to a pH value = 3 decreases the extent of adsorption of sodium poly(methacrylic acid). A decrease in adsorption after a pH change was observed when using the zeolite CBV-780 and water pH = 3, i.e., the polymer was partially eluted (Fig. 3). Data for columns packed with zeolite CBV-780 and CP814E in water at pH = 10 could not be obtained due to very high (>250 bar) column back pressure. Repeated packing of the columns with new sorbents did not lead to smaller back pressure. We suppose that the small particles of these sorbents strongly agglomerate in this mobile phase. These columns also had a higher resistance in water with pH = 3.

Assuming that a solvated macromolecule has a hypothetical spherical shape, it is possible to calculate the corresponding radius of this sphere, denoted as radius of gyration, R_g. In Table 2, the hydrodynamic radii of PEO in three solvents are presented. They were calculated according to relations, which were recently described.[18] The results depend on the values of constants a, K from the Mark-Houwink-Sakurada equation, therefore, they are also included in Table 2. It is clear that the polymer coils do not fit into the pores the zeolites used for analysis. On the other hand, after a change in conformation from random coils to an approximately linear conformation, PEO chains could enter the pores. We have observed the full retention of polymers, when good solvents for polymers were used. Such solvents support the conformational changes of the polymer chains. After the conformational change, macromolecules should have smaller critical diameters than the size of the pores. The corresponding calculated critical diameters are summarized in Table 3.

According to the calculated critical diameters in Table 3, it seems that when pores in the zeolite are smaller than the critical diameter of the polymer, i.e., the polymer chain cannot enter into pores, then the polymer is not retained in the zeolite. For example, PPG and sodium poly(methacrylic acid) are retained only in zeolites with larger pores (CBV-780, CP 814E). Polymers with smaller critical diameters (PEG, PEO, PVA) are adsorbed onto all tested zeolites, if a suitable solvent is selected.

As is shown in Tables 2 and 3, the difference between the pore sizes and the critical diameters of solvent and polymers is small. As a result, adsorbed molecules of polymer or solvent may block the pore entrances. This may prevent the desorption of adsorbed polymers or, make it even impossible.

Table 2. The calculated radius of gyration for polyethylene oxide.

Mobile phase	Polyethylene oxide					
	T (°C)	a	K (mL/g)	Ref.	M (g/mol)	R_g (Å)
Water	30	0.78	0.0125	[32]	1,500	12.2
					27,500	68.5
					545,000	403.1
Acetone	25	0.67	0.032	[33]	1,500	12.7
					27,500	64.4
					545,000	339.8
Methanol	25	0.57	0.0852	[34]	1,500	13.8
					27,500	63.5
					545,000	303.2

Table 3. Critical diameters of polymers and solvents.

Substance	Critical diameter (Å)
Polyethylene oxide	5.04
Polyethylene glycol	5.04
Polypropylene glycol	5.41
Polyvinyl alcohol	4.80
Sodium poly(methacrylic acid)	6.48
Acetone	5.51
Methanol	4.34
Water	3.18
Diethylene glycol monobutyl ether	5.67

Buttersack et al.[14] have shown that dextran and PEO were adsorbed from the aqueous phase on an FAU-type zeolite, although hydrodynamic diameters of the polymers in the mobile phase were up to 32 times larger than the pore diameter of the zeolite. Grüll et al.[25] have measured the adsorption equilibrium of PEO from water on porous glass, and Berek, Tarbajovska [35] have determined elution volumes of PEO from tetrahydrofuran and tetrahydrofuran/dimethylformamide on silica gel C18 (with average pore diameter 100 Å). All three groups[14,25,35] concluded that macromolecules, which in principle should be sterically fully excluded from the pores, taking into account the hydrodynamic diameters of the macromolecules, change their conformation and partially penetrate into the pore volume. This assumption was supported by theoretical Monte Carlo simulations of macromolecular chains in model pores.[36–38] The calculations[36,37] have shown that one part of the macromolecular chain could be adsorbed inside of the pores and the second part at the pore mouth, when the loss of conformational entropy of macromolecules is surmounted by the large gain in enthalpy. The de-coiled part of the macromolecule, which enters a narrow pore, looks like a stem, while the rest of the coil resembles the crown of a flower ("flower-like conformation"[36,37]).

Skrinarova et al.[38] have examined the partitioning of flexible macromolecules into adsorptive pores under good solvent conditions by simulations. Their results indicate that pulling of chains into pores by attractive walls becomes more effective in narrow slits, i.e., the retention of macromolecules was indirectly proportional to the pore dimensions, when the pore-wall attraction was the driving force of the chain penetration into the pore. The model calculations for the ratio $2R_g$/pore diameter > 1 were, however, not yet performed.

We assume that the polymers studied here may also partially diffuse into the narrow pores of zeolites and adsorb in the flower-like conformation.

If a PEO or a PEG molecule would be adsorbed as a coil, then, naturally, the number of ether groups in contact with the adsorbent would be small. In the case of a straightening of the macromolecular coils in narrow pores, all parts of the macromolecule inside of the pore are in contact with the adsorption centers. The pore sizes in zeolites used in this work are about 12–16 smaller than the pores in the porous glass[25] and silica gels C18.[35] An increase in the heat of adsorption as the pore diameter decreases is widely accepted to be true,[39–41] i.e., the adsorption potential in smaller pores is larger than in larger pores. The overlapping of the adsorption potential within the narrow channels of zeolite crystals, made up of van der Waals and electrostatic forces, strengthens the energetic interaction of the adsorbed molecules with the solid phase.[42] Thus, very pronounced retention may occur in the case that a sorbate enters into micropores (pore sizes $<20\,\text{Å}$).

It is known that a polymer may be fully adsorbed on a sorbent from a very good thermodynamically single solvent.[43] Such adsorption systems were up to now, however, quite rarely found. For example, PEO is adsorbed from water on porous glass[25] and carbon black,[44] from benzene on silica,[45] from tetrachloromethane on nonporous silica,[26] and PEG is adsorbed from water on carbon black.[45] As shown here, using zeolites, i.e., sorbents with very narrow pore diameters, polymers were strongly adsorbed from several thermodynamically very good solvents.

CONCLUSION

Chromatographic behavior of several synthetic polar water-soluble polymers on zeolite column packings was studied. A full retention of the polymers was found in several chromatographic systems zeolite-mobile phase. In addition to full retardation of the polymers in the zeolite column packings, a partial elution of polymer samples was observed in some systems.

According to our knowledge, this is the first paper dealing with a chromatographic behavior of synthetic polar water-soluble polymers within microporous column packings.

Hydrodynamic diameters of the polymer coils in solution are about 2–80 times larger than the pore size in the zeolites. Thus, solvated macromolecules should be sterically excluded from the pores. We propose a mechanism in which the polymer coils change their conformations from the random coils to prolonged shapes, and partially penetrate into the narrow zeolite pores. Penetration of the chains into the pores occurs due to attractive interactions between the polymer chain and the surface of the zeolites inside the pores. Inside the narrow pores these interactions may be much more intensive than in large pores or on the surface of sorbent particles.

Full adsorption of synthetic polymers on zeolites was observed in studies of the adsorption equilibrium under static conditions,[14] as well as by chromatographic measurements (here and in Ref.[18]). As a rule, polymers were adsorbed from thermodynamically very good solvents. Such solvents are selected, when desorption of the polymers from a sorbent is needed. This illustrates the unusual large affinity of polymers to the microporous sorbents.

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