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Investigations on the selectivity of grafted high performance anion exchangers and the underlying graft mechanism

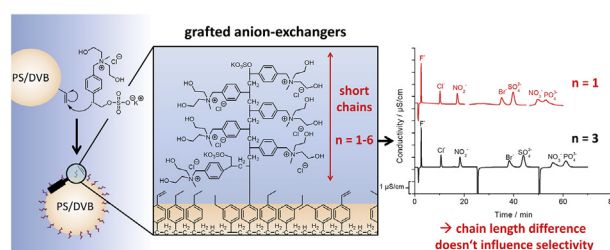
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HIGHLIGHTS

- Anion exchangers have been prepared using free radical graft polymerization and a molecularly predefined ion exchange site.
- A link between the graft conditions and resulting ion exchange selectivity has been found.
- Concepts of “local capacity” and “grafting from” or “grafting onto” are used to explain selectivity and performance changes.

GRAPHICAL ABSTRACT



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ABSTRACT

Macroporous, monodisperse PS/DVB particles with diameters of 4.0–4.6 μm were functionalized via free radical graft polymerization to create high performance anion exchangers. Varying the amount of monomer from 0 to 10 mmol per 2.0 g PS/DVB allows a control of the column capacity to create columns with capacities up to 350 $\mu\text{eq}/\text{column}$ for 100 mm columns. No further increase of the capacity is observed when using more than 6 mmol of the monomer due to a rivaling homopolymerization. With increasing capacity, the exchangers showed increasing selectivity factors of Br^- and NO_3^- in reference to Cl^- from 2.4 to 4.3 and 3.5 to 4.6, changing the elution order in the process. At the same time, contradicting the retention model, the selectivity of SO_4^{2-} did not change with increasing capacity. Analyzing the amount of converted double bonds during functionalization allowed to identify a grafting-onto mechanism, as the amount of converted double bonds ranges from 0% to 52% depending on the amount of monomer used. This information also allowed the calculation of the average chain length, which ranges from 1 to 6 exchanger groups. The average chain length depends on the amount of monomer used, creating higher average chain lengths with higher amounts of monomer. However, it was not possible to link the observed selectivity differences to the average chain lengths of the columns or the influence of the column capacity on the ion exchange mechanism.

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1. Introduction

Ion chromatography (IC) has evolved to be an important method to analyze a wide range of inorganic and small organic ions since its

development by Small et al. in 1975 [1] and further development of its application by Gjerde, Fritz and Schmuckler [2–4]. Therefore, the development of IC columns has attracted a lot of attention. It is desirable to create IC columns with high performance, fast separations and steerable selectivity, so versatile columns or columns with a specific selectivity can be obtained [5–9]. Controlling the selectivity of a column is a difficult task that depends highly on the

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construction principle of the stationary phase [10–12]. Therefore, most commercial columns show very specific application areas instead of broad fields of applicability [13–15].

IC stationary phases are primarily created by functionalization of a substrate with a functional group or a functional layer containing the ion exchange groups. Typically organic polymers like polyvinylalcohols [16,17], polymethacrylates [18,19] as well as crosslinked ethylvinylbenzene-divinylbenzene (EVB-DVB) or polystyrene-divinylbenzene (PS/DVB) [20,21] are used as substrates because of their pH stability. The less stable silica phases are also used [22], but offer restricted applicability. Functionalization is either achieved by binding the functionalization covalently or non-covalently, e.g. by using electrostatic [23–25] or hydrophobic [26–28] interactions. A wide range of covalent functionalization methods exists, ranging from direct attachment of the exchanger group onto the substrate surface [29,30] to “hyperbranched” structures by using step-growth polymer on top of the substrate surface [20,21,31].

1.1. Graft-polymerization

Graft-polymerization is a versatile way to create covalently bonded anion exchangers by attaching a polymer chain, containing the exchanger groups or a precursor allowing further functionalization, on top of a polymer substrate [32–34]. This allows the creation of pellicular structures, resulting in high separation efficiencies [5]. The first application of graft-polymerization to create IC stationary phases can be dated back to 1991 when Schomburg et al. grafted cation exchangers onto polymercoated silica particles [35]. Until today different methods are applied to create grafted ion exchangers, with atom transfer radical polymerization (ATRP) being widely-used [5,36,37]. Dionex already offers grafted anion columns like the IonPac AS14 and the IonPac AS14A. Those columns are based on EVB/DVB particles functionalized with methacrylate-based functional groups via graft or block-graft polymerization [38]. Nevertheless other graft methods, like the free radical polymerization, can be used for functionalization. A free radical polymerization is difficult to control, but can be directly applied to PS/DVB or EVB/DVB without the need of substrate modification [39]. In addition the reaction is easy to perform and allows a fast preparation of ion exchangers. For use with PS/DVB or EVB/DVB a radical initiator like potassium persulfate is used to generate radicals that initiate the graft-polymerization.

Three types of reaction mechanism can occur in graft-polymerization [40]. In case of the “grafting-from” mechanism the radical initiator generates a radical on top of the PS/DVB or EVB/DVB surface. Afterwards the monomer is grafted on top of the PS/DVB surface. The second mechanism is the “grafting-onto” mechanism. Instead of initiating the polymerization on top of the PS/DVB or EVB/DVB surface, the radical initiator reacts with the monomer to generate a monomer-radical. This monomer-radical then reacts with the PS/DVB or EVB/DVB surface and initiates the graft-polymerization. The last possible mechanism is called “grafting-through” mechanism. The radical initiator starts a homopolymerization of the monomer. The homopolymer then reacts with the PS/DVB or EVB/DVB surface to generate the grafted polymer.

1.2. Selectivity of anion exchangers

Generally when creating a column, a specific selectivity is generated for a defined area of application. This means a specific elution order has to be achieved. To learn more about how to influence the selectivity of a column, small changes in the selectivity have to be taken into account. For quantification of those changes the selectivity factor α of two analytes is calculated from their

retention factors k . The selectivity factors of the same analytes can then be compared for different columns to investigate influences on the selectivity. Equation (1) shows the calculation of α where $k(B) > k(A)$ is given.

$$\alpha_{B,A} = \frac{k(B)}{k(A)} \quad (1)$$

To control the selectivity of a column it is important to identify the key players that influence on the selectivity. The first obvious key player is the ion exchange process. A retention model [3,41,42] shows those possibilities to change the retention factor k of an analyte. Therefore, it gives insights on how to render the column selectivity due to the ion exchange process. Equation (2) shows the dependency of k for an analyte A on the effective charge of the analyte x_A and of the eluent ion y , the equilibrium constant $K_{A,E}$, the exchanger capacity Q , the phase-volume ratio Φ and lastly the eluent concentration $c(E^{y-})$.

$$k(A) = (K_{A,E})^{\frac{1}{y}} \cdot \left(\frac{Q}{y}\right)^{\frac{x_A}{y}} \cdot \Phi \cdot c(E^{y-})^{-\frac{x_A}{y}} \quad (2)$$

Equation (2) can be applied to equation (1) to get the following term:

$$\alpha_{B,A} = \frac{(K_{B,E})^{\frac{1}{y}} \cdot \left(\frac{Q}{y}\right)^{\frac{x_B}{y}} \cdot \Phi \cdot c(E^{y-})^{-\frac{x_B}{y}}}{(K_{A,E})^{\frac{1}{y}} \cdot \left(\frac{Q}{y}\right)^{\frac{x_A}{y}} \cdot \Phi \cdot c(E^{y-})^{-\frac{x_A}{y}}} \quad (3)$$

This can be simplified to:

$$\alpha_{B,A} = \left(\frac{K_{B,E}}{K_{A,E}}\right)^{\frac{1}{y}} \cdot \left(\frac{Q}{y}\right)^{\frac{x_B-x_A}{y}} \cdot c(E^{y-})^{\frac{x_A-x_B}{y}} \quad (4)$$

The selectivity still depends on various factors, but for the special case that x_A equals x_B the equation can be simplified even further:

$$\alpha_{B,A} = \left(\frac{K_{B,E}}{K_{A,E}}\right)^{\frac{1}{y}} \quad (5)$$

This also means that changes of the column capacity Q or the eluent concentration $c(E^{y-})$ only have a very small influence on the selectivity of two analytes with similar effective charges. Furthermore equation (4) shows that the influence of Q and $c(E^{y-})$ on the selectivity increases strongly when there are differences in x_A and x_B . Therefore, to compare the selectivity of analytes on two different columns, it is important to keep in mind that differences in the capacities of those columns can be a reason for different selectivities.

The theory of the ion exchange process gives us three possibilities to influence the selectivity of a column. Modifying the equilibrium constants of the analytes is the most promising but at the same time most complicated way. The equilibrium constants can be influenced by the functional group used as exchange group, by matrix effects caused by the polymer or by components of the eluent. Varying the ammonium-substituents results in different selectivities of the corresponding ion exchangers, because the hydration of the exchange group is affected [43–46]. It was shown that OH^- shows a very distinct selectivity if alkanolammonium groups are used [46]. Recent investigations on hyperbranched exchangers show a strong influence of the number of modification cycles, side reactions [47], the branching degree [21] as well as the quaternizing agent [48] on the selectivity of the resulting exchangers. In addition, negatively charged groups inside the layers

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