Preparation and characterisation of anion exchangers with dihydroxy-containing alkyl substitutes in the quaternary ammonium functional groups

A.V. Zatirakha [a],[*], A.D. Smolenkov [a], A.V. Pirogov [a], P.N. Nesterenko [b], O.A. Shpigun [a]

[a] Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1/3, GSP-1, Moscow 119991, Russia
[b] Australian Centre for Research on Separation Science (ACROSS), University of Tasmania, Hobart 7001, Australia

ABSTRACT

Novel poly(styrene-divinylbenzene) (PS-DVB) based anion exchangers having one and two (2,3-dihydroxypropyl) substitutes in the quaternary ammonium functional groups are prepared and characterised by ion chromatography (IC). The introduction of bulky and hydrophilic substitutes to the anion-exchange groups allows the elimination of non-ionic interactions between the polarisable anions and the aromatic rings from the matrix and the improvement of separation selectivity as compared with the traditional trimethylammonium (TMA) functionalised ion exchangers. The synthesis of the ion exchangers includes acylation of PS-DVB particles with acetic anhydride followed by reductive amination either with methylamine hydrochloride or dimethylamine and further alkylation with oxiranes under varied conditions. The ion exchange selectivity and separation efficiency of nine adsorbents having different structure of bonded groups, ion exchange capacity (9–98 μequiv. g^{-1}) or particle size is studied for model mixture of inorganic anions (F$^-$, Cl$^-$, NO$_2^-$, Br$^-$, NO$_3^-$, HPO$_4^{2-}$ and SO$_4^{2-}$) using carbonate and hydroxide eluents. The adsorbents with more hydrophilic substitutes provided superior columns efficiencies and better peak symmetry as compared with analogues having hydrophobic functional groups. The calculated values of column efficiencies for polarisable NO$_3^-$ and HPO$_4^{2-}$ are 18,500 and 29,000 N/m, respectively, for anion-exchanger, having *N*-methyl-*N'*,*N''*-di-(2,3-dihydroxypropyl)ammonium groups which is significantly higher than 1800 and 12,000 N/m obtained for these anions with anion exchanger bearing TMA functional groups.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

In the last decade a remarkable progress in the development of ion chromatography (IC) was noted. The recent achievements in IC are associated with introduction of new separation media such as capillary [1–3] or monolithic columns [4,5], and columns packed with particulate ion-exchangers having smaller diameter of particles [6] or advanced core shell structure [7]. It leads to dramatic increase in the speed and resolution of separations and improves sensitivity of IC. However, the development of new selective anion-exchangers remains an important task in development of IC [6,8–11]. The column efficiency in IC depends predictably on common for LC parameters like matrix type [12], particles size and their distribution on size [6,13], packing procedure [14], etc., but anion-exchange selectivity is defined by much more complex

surface chemistry [9,10,15] and in some extent by the eluent composition and column temperature.

Poly(styrene-divinylbenzene) (PS-DVB) is a common matrix for the preparation of the anion exchangers due to its chemical stability in the broad pH range (0–14), low swelling/shrinking under variation in the eluent concentration, good compatibility with polar organic solvents and sufficient mechanical strength allowing the use of micro particles as column packing. There are few papers on the modification of anion-exchange selectivity by changing the structure of the functional groups in PS-DVB based anion-exchangers [16–19].

In their early work Fritz and Barron [20] studied the retention of inorganic anions on the ion-exchange resins prepared by amination of chloromethylated PS-DVB resin with various amines. The authors noted that the replacement of one or more alkyl fragments in the functional group of the anion-exchanger (Type I anion-exchange resin) with more polar substituent (Type II anion-exchange resins) has a dramatic effect on the selectivity. For example, dimethylethanolammonium (DMEA) functionalised resin shows much lower affinity for common inorganic anions comparatively to OH$^-$ than the ion-exchanger containing TMA groups.

Later, the authors found that the use of *tri*-n-alkylamines with long alkyl substitutes for amination of chloromethylated PS-DVB improves significantly the ion-exchange selectivity of the resins, but it causes a stronger retention and deterioration of the chromatographic peaks of polarisable anions [20,21]. This effect is attributed to the increase in the hydrophobicity and bulkiness of the functional groups making more favorable interactions with polarisable anions in aqueous eluents according to "water-structure induced ion-pairing" theory [22]. Ion-exchange selectivity of PS-DVB based anion-exchanger also depends on the length of the linker between the bonded TMA groups and the surface of PS-DVB particles [15,23]. The relative retentions (t_R^{An}/t_R^{Cl}) of double charged and weak acid anions are independent on length of linker (C_1–C_6 atoms), but relative retentions for polarisable anions (ClO_3^-, NO_3^-, I^-) decrease with increased distance between TMA group and PS-DVB surface. The increase of the surface concentration of TMA groups (C_3 linker) from 35 to 73 μmol g^{-1} increases t_R^{An}/t_R^{Cl} values for Br^-, ClO_3^-, NO_3^-, I^- and $S_2O_3^{2-}$ and has no effect on retention of SO_4^{2-} [23].

Slingsby and Pohl [17] compared the ion-exchange selectivity of the agglomerated anion-exchangers coated with poly(vinylbenzylchloride) based latex containing methyldiethanolammonium (MDEA), DMEA, TMA and triethylammonium (TEA) functional groups. They found that alkanolammonium latices have the enhanced affinity for OH^- as compared with the trialkylammonium ones, therefore, the retention factors (k) decreased in case of more hydrophilic anion-exchange sites with hydroxide eluent. Using 5 mM Na_2CO_3 as the eluent the authors observed the remarkable increase of the k values for the polarisable anions with increasing the hydrophobicity of the anion-exchange groups. For TMA and TEA functionalised anion-exchangers the retention of polarisable NO_3^- and Br^- was much stronger than that of HPO_4^{2-} and SO_4^{2-}, while the MDEA modified resin having two hydroxyls in the anion-exchange site showed the lowest affinity for the double charged anions.

Bruzzoniti et al. [16] compared the ion-exchange selectivity of three ethylvinylbenzene-DVB based agglomerated type anion-exchangers coated with latex particles containing zero, one and two hydroxyl groups in the alkyl amine functional sites for the separation of F^-, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} using hydroxide eluent. The results showed an increased affinity of anion-exchangers for OH^- ions from the eluent with the increase in the number of hydroxyl groups in the functional site. Again, the k values increased for all anions with remarkable changes noted for NO_3^- and double charged SO_4^{2-} and HPO_4^{2-}.

The specific interactions between polarisable anions and anion-exchange resin including van der Waals [11,16], π–π [17,24,25], anion-π [26,27] and other interactions [15] may be responsible for some unwanted effects in IC separation such as extra peak broadening, deterioration of peaks and very strong retention of selected anions. The possible solution of this problem may be achieved by increasing the hydrophilicity of the ion exchange functional groups. For this purpose the authors proposed using various amines for the amination of chlomethylated PS-DVB matrix. The increase of the column efficiency together with decrease in the relative retention and the improvement of peak symmetry for polarisable anions was reported for 1,1-dimethylhydrazine functionalised resin [19]. More recently, the promising results were obtained for PS-DVB based anion-exchanger having hydrophilic functional groups prepared by the introduction of the tertiary amino groups followed by alkylation with epichlorohydrin and glycidol [28,29].

The aim of this work included the development of the new scheme for the functionalisation of PS-DVB micro particles with the bulky hydrophilic quaternary ammonium groups via short C1 linker and the characterisation of the ion-exchange selectivity and chromatographic performance of the prepared anion-exchangers.

2. Experimental

2.1. Instrumentation

"Memmert" Thermostate (Memmert GmbH, Schwabach, Germany), "Laboport" vacuum pump (KNF Neuberger, Tranton, NJ, USA), "Sapphire 6580" ultrasonic bath (Sapphire, Moscow, Russia), "Eurostar" mechanical stirrer (IKA-Werke, Staufen, Germany) were used for the syntheses.

A Dionex ICS 3000 Ion Chromatography system (Dionex part of Thermo Scientific, Sunnyvale, CA, USA) comprised a gradient pump, an autosampler and a conductimetric detector with an ion suppressor was used for IC with sodium hydroxide as an eluent. A Stayer Chromatography IC system (Akvilon, Moscow, Russia) equipped with an isocratic pump and a conductimetric detector CD-510 with an ion supressor Emsec 21 was used for IC with carbonate and bicarbonate eluents. Data acquisition and processing were controlled by Chromeleon 6.8 (Dionex) and Multichrom 1.5 (Ampersand, Moscow, Russia) software packages, respectively. The 50 mm × 4.0 mm I.D. stainless steel columns were used as a housing for all the studied adsorbents and slurry packed at 200 bar using K-1900 pump (Knauer, Berlin, Germany). The hydrophilicities of the functional groups were calculated with the use of EPIWEB 4.11 software [30].

2.2. Reagents

All chemicals had reagent and analytical-reagent grade and were purchased from Sigma–Aldrich (Moscow, Russia). PS-DVB microspherical particles (cross-linking degree of 25%, particle size 3.3 ± 0.2 μm, 200 m^2/g, pore volume 0.64 cm^3/g) were synthesised in the laboratory as previously described [31]. PS-DVB microspherical particles (particle size 7 μm, pore size 10 nm) of Polymer X (Phenomenex, Torrance, CA, USA) were also used for the preparation and the comparison of the anion-exchangers.

2.3. Synthesis of anion exchangers

The structures of all the obtained anion-exchangers are presented in Table 1 and scheme of the synthesis is shown in Fig. 1. The synthesis was performed on the loose polymers as described [28] with slightly modified procedures for the reductive amination and alkylation steps in the case of the anion-exchangers having the structure **III**, which will be discussed later in Section 3.2. The packing procedure was provided using 0.1 M NaOH as a solvent for both preparing the slurry and the driving solution. Anion exchange capacities of the columns were measured by the saturation with 20 mM Na_2SO_4 followed by the elution of adsorbed sulphate with 2 mM Na_2CO_3 and the quantitative IC determination in the collected volume of effluent using a Dionex IonPac AS11 column.

3. Results and discussion

3.1. Synthesis

There are several methods suitable for the preparation of the anion exchangers including chloromethylation [20,32], Friedel–Crafts acylation [33–35] and alkylation [23] of PS-DVB matrix followed by amination. As a rule, amination of chloromethylated PS-DVB with alkylethanolamines is used for the synthesis of anion-exchanger bearing hydrophilic ion exchange groups [16–19]. Alternatively, the alkylation of the tertiary amino groups at the surface of PS-DVB particles with epichlorohydrin and glycidol [28,29] can be used as a simple way of obtaining the quaternary ammonium structures with long hydrophilic alkyl substituent e.g. anion-exchanger **II** in Table 1. Improvements in both column