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Characterization of ion exchange functionalized cyclic olefin polymer open tubular columns

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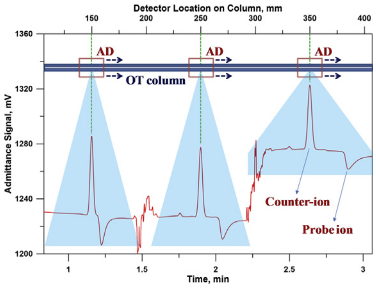
HIGHLIGHTS

- Ion-exchange capacities in nano-equivalents measured accurately by titrimetry.
- Frontal displacement produces lower capacities than acid/base titrimetry.
- Capacity nonuniformity along a column is readily measurable.
- Anion exchange latex coating provides relatively uniform surface functionalization.

GRAPHICAL ABSTRACT



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ABSTRACT

We describe both the cation-exchange (CEX) and anion-exchange (AEX) capacity measurements of functionalized cyclic olefin polymer (COP) open tubular (OT) columns. COP capillaries were sulfonated to provide CEX functionality and then coated with AEX latex to provide AEX functionality. We measure functionalization uniformity along the column by (a) separately measuring capacities of two halves of a column, (b) measuring retention factors for several ions in successive 10 cm segments of a column in multiple injections and (c) measuring retention variance of a single ion in different segments of a column from a single injection. Data were collected in both flow directions. Errors in CEX capacity determination arises primarily from uncertainties in titration end point location. AEX capacities are typically 10x higher, reducing the relative measurement error. In the AEX case, both titration end point location error and variations in column internal diameter contribute to the overall uncertainty. Although sulfonation of COP results in nonuniform CEX functionalization, AEX latex coating of this surface results in uniform AEX coverage. Frontal displacement chromatography (using both admittance and optical detection) and acid-base titrimetry were compared for capacity measurement. In a pooled standard deviation based *t*-test for the data on 8 columns, at the 95% confidence level, CEX capacity differed significantly between two halves of a column. But AEX capacity of AEX columns prepared by coating the same CEX columns with AEX latex did not.

1. Introduction

Open tubular liquid chromatography (OTLC) was first proposed by Nota et al. [1]. Jorgenson et al. [2] pointed out the bottleneck to be suitable detectors. Despite efforts towards detectors [3], and higher capacity columns [4], OTLC is far from routine. On the other hand, because of availability of a suitable detector, the situation may be different for open tubular ion chromatography (OTIC).

Solution impedance measurement in a capillary was introduced in 1998 [5,6] and soon termed Capacitively Coupled Contactless

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Conductivity Detection (C^4D). The detector really measures the inter-electrode impedance, controlled both by the wall capacitance as well as the capacitance and resistance of the solution [7]. Recent work has shown lower frequencies to be of benefit for small diameter columns and/or high resistivity solutions. Sensitive detection of ions has become readily and inexpensively possible even in 5 μm ϕ capillaries [8,9]. Both suppressed and non-suppressed high efficiency OTIC systems have now been demonstrated [10,11].

Packed macroscale IC columns often rely on positively charged (AEX) latex nanoparticles electrostatically attached to a negatively charged substrate. Either carboxylated and sulfonated substrates work, but in OTIC, experience indicates that only a sulfonated surface binds to positively charged latex particles strongly enough to resist wash-off by a strongly alkaline eluent. Of silica, poly (methylmethacrylate) (PMMA) and cyclic olefin polymers (COP) studied thus far, only COP could be functionalized with base hydrolysis resistant sulfonate groups. This manuscript therefore addresses only COP based columns.

With simple, sensitive, and universal detection for ions in hand, there is thus hope that OTIC may become the first subset of OTLC to come into practical use. In these early days of OTIC, measurement methods for ion exchange (IEX) capacities (typically of the order of nanoequivalents (neq)/column) and their limitations are not well established. While OTIC is still at an early stage, we document here the present status of column characterization. In traditional LC/IC, column longitudinal uniformity is generally unknown. Admittance detection enables imaging a non-metallic column from the outside. We therefore also report on column uniformity.

2. Perspective

2.1. Ion exchange capacity of open tubular columns

We recently compared the capacity parameters and retention behavior of OT vs. packed IC columns [12]. OT IEX capacities are minuscule and difficult to measure: very few reports on OT IEX capacities exist. Ishii and Takeuchi [13] sulfophenylsilylated a surface-etched glass column (0.060 × 5400 mm); NaCl solution was then passed through the H^+-form column. The liberated HCl was measured to be 108 neq by microtitration with NaOH (coverage 106 peq/mm^2). Pirogov and Buchberger coated a 0.100 × 500 mm silica capillary with 3-x-ionene bromide [14]. Bromide released by sulfate displacement amounted to 2.5 neq (coverage 16 peq/mm^2); the surface area based estimate was 10 neq. Most OT IEX columns since characterized were prepared by latex attachment as detailed below.

2.2. Latex coated open tubular columns

Most surfaces are intrinsically negatively charged, positively charged latex particles can be attached to them electrostatically. Such columns were used for OTIC early [15]. Electron microscopic studies have suggested a monolayer latex coverage [16]. Hutchinson et al. [17] theoretically estimated, and experimentally determined, the AEX capacities (C_{AEX}) of latex coated and silica-based monoliths made in 50–75 μm silica capillaries. Estimates were based on specific capacity of latex particles, volume of individual particles assuming cubic morphology and monolayer coverage. Electron micrographs [16] indicate some latex agglomeration; this would increase the observed capacity compared to a monolayer assumption. Assuming cubic rather than spherical morphology of latex particles in part compensates for this. Hutchinson et al. [17] measured capacity of OT columns by frontally displacing specific UV-absorbing anion loaded columns with perchlorate. For 0.025 × 250 mm columns coated with AS5A latex (specific capacity 12 μeq/g, 70 nm dia.), C_{AEX} for IO_3^-, Br^-, NO_3^-, I^-, SCN^-, CrO_4^{2-} were determined to be 1.9, 7.3, 12.1, 14.0, 15.6 and 16.5 peq (coverage range 0.1–0.8 peq/mm^2), respectively (data courtesy of E. F. Hilder, Univ. South Australia).

2.3. Is ion exchange capacity a definitive term?

The ion exchange capacity (C_{IEX}) of an IEX phase is thought to be a definitive term. The ~8x dependence of C_{AEX} above on the anion chosen is cause for reflection. Even manufacturer measurement methods for C_{IEX} in commercial IC columns differ: one vendor measures CEX capacity (C_{CEX}) and C_{AEX} by measuring the respective amounts of K^+ and Cl^- displaced from a KCl-loaded column; these capacities tend to be lower than those determined by acid-base titrations [18]. Neither really provides C_{IEX} under use conditions; there may not be a single universally accurate C_{IEX} value of a column. Converting an AEX/CEX column with strong base/acid, and then determining the amount of captured OH^-/H^+ by titrating with strong acid/base provides essentially the maximum capacity value. Such a measurement weighs both strong/weak acidic/basic groups equally. Do the weakly basic AEX sites play any role in high pH hydroxide eluent separations? Is the chloride binding capacity of the same column equilibrated with a KCl solution more appropriate? Should one determine the chloride binding capacity in the same hydroxide eluent? How relevant is that value if perchlorate is to be determined?

2.4. OT IEX capacity measurements

As previously stated, latex attachment to silica or PMMA OT columns is lost in strong base [19]. For AEX latex attached to PMMA, C_{AEX} could be determined by (a) loading the column with fluorescein anion, washing, displacing with excess Na_2SO_4 and measuring the liberated fluorescein offline; (b) loading the column with easily displaced iodate, washing and displacing with a standard chloride solution (frontal displacement chromatography, FDC) with either on-column absorbance or admittance detection to discern onset of iodate elution.

Sulfonation of COP capillaries results in a strongly acidic surface that provides base-stable AEX latex attachment [20] and enables on-column acid-base titration to measure C_{AEX}. This can be compared to measurements by neutral-pH FDC methods. Chromatographic behavior of sulfonated COP depends on the degree of sulfonation. A highly sulfonated wall exhibits ion exclusion behavior, e.g., the ability to separate water and ethanol. Although C_{AEX} after AEX latex coating is not much affected by the underlying C_{CEX}, only low-C_{CEX} AEX columns do not show ion exclusion effects [20]. A complete characterization of such columns thus includes the measurement of C_{CEX} and C_{AEX}, after sulfonation and after AEX latex coating, respectively. To avoid ion exclusion effects, a low C_{CEX} value (~< 3 peq/mm^2) is preferred, this is typically ~10x lower than C_{AEX} and is thus more difficult to measure.

3. Experimental section

3.1. Reagents and materials

Zeonex 330R (www.zeonex.com) pellets were vacuum degassed while molten in rectangular containers. Cylindrical ingots, one 92.7 mm and the other 62.4 mm in outer diameter, ca. 30 cm long, were machined therefrom in our laboratory. A 4.76 mm (3/16 in.) concentric hole was drilled axially to make the preforms with o.d./i.d. aspect ratios of 19.5 and 13.1, respectively. The preforms were extruded (www.paradigmoptics.com) to make the final tubing; the i.d./o.d. ratio remains approximately constant from the preform to

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