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Chromatographic behaviour of synthetic high pressure high temperature diamond in aqueous normal phase chromatography

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ABSTRACT

The chromatographic properties of high pressure high temperature synthesised diamond (HPHT) are investigated under the conditions of hydrophilic interaction liquid chromatography (HILIC). A 50 × 4.6 mm ID stainless steel column packed with HPHT particles of mean diameter 1.6 μm and specific surface area 5.1 $m^2 g^{-1}$ is used. According to the results of acid-base titration with NaOH the purified HPHT batch contains 4.59 μeq g^{-1} of protogenic, mainly carboxyl- and hydroxyl-, groups, which make this polar adsorbent suitable for use as a stationary phase in HILIC. The retention behaviour of several classes of polar compounds including benzoic and benzenesulfonic acids, nitro- and chlorophenols, various organic bases, and quaternary ammonium compounds are studied using acetonitrile and methanol based mobile phases containing 5–30 v/v% of water. The effects of the buffer pH and concentration, column temperature and organic solvent content on retention of model compounds are also investigated. It is shown that both pH and acetonitrile/methanol ratio in the mobile phase can be used to vary the separation selectivity. Molecular adsorption mechanism (related to aqueous normal phase mode), rather than partitioning is established to be responsible for the retention.

1. Introduction

In recent years, the emergence of new methods for preparation of diamond, nanodiamond and other carbon materials has resulted in their greater availability, and this has intensified research on their possible exploitation in a wide range of applications. Excellent thermal, chemical and mechanical stability, along with the unique surface chemistry of diamond-based materials, makes them especially advantageous for application in chromatography as a stationary phase [1,2]. Over the last decade several research groups have investigated the potential of using diamond based stationary phases in various modes of liquid chromatography and their benefits and drawbacks as compared to conventional silica and polymeric materials [3–11].

Great diversity in the available diamond and nanodiamond materials, amplified by variations in their surface properties based on synthesis and purification procedures, makes it hard to compare results obtained by different research groups. Therefore, to fully understand the chromatographic properties of this complex material, it is of foremost importance to understand the chromatographic properties of simple unmodified diamond particles, such as high pressure high temperature (HPHT) diamond [3]. Performance of such material can later be used as a reference for comparison with other diamond based stationary phases. As it was shown previously, HPHT diamond possesses a hydrophilic surface with a high content of hydroxyl, carbonyl and carboxyl groups [2]. Accordingly, it was applied in normal phase (NP) high performance liquid chromatography (HPLC) and exhibited retention for various classes of solutes with polar functional groups [2]. NP-HPLC involves the use of a polar stationary phase and a less polar mobile phase. Therefore, in this paper it was decided to investigate the behaviour of the HPHT diamond column in other variants of NP-HPLC, namely aqueous normal phase (ANP) and hydrophilic interaction liquid chromatography (HILIC).

The majority of ANP and HILIC applications use water-acetonitrile mobile phases, with a high (≥70%) content of organic solvent [12], providing substantial retention for polar analytes with all suitable stationary phases. Generally it is accepted for both modes that hydrophilic interactions are responsible for retention, and the main difference between these two modes being within the precise retention mechanism. In HILIC, retention occurs due to the partitioning of solutes between the water-enriched layer at the polar surface of the sorbent, and the bulk mobile phase [13], in a similar way to RP-HPLC, where the partitioning occurs between the

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ACN-enriched surface layer and the bulk of the eluent [13,14]. ANP is a variation of adsorption chromatography, where the adsorption occurs due to hydrogen bonding, ion-exchange and dipole–dipole interactions [15,16].

The use of other water soluble solvents, including both aprotic acetone [17–21], ethylacetate [17], tetrahydrofuran [22–25], dimethylformamide [26], dioxane [26] and protic methanol [18,22–25,27], ethanol [18,27], 1-propanol [26] and 2-propanol [18,22–25,27] as possible alternatives to acetonitrile-water mobile phases for HILIC and ANP have been studied. Among these solvents, only acetone containing mobile phases provided similar levels of retention in HILIC, while addition of other solvents decreased the retention times on diol-, polyol-, amido- and bare silica stationary phases [28]. However, the effect of the organic solvents, especially alcohols, on both retention and separation selectivity is more profound for stationary phases having ion-exchange groups, such as zwitterionic (ZIC phase) [26,27], aminopropyl- [17,23,25,27] and tetraethylenepentamino- modified silica [18], and, to a lesser extent, silanols in bare silica [19,23,24]. The use of alcohol-water mixtures can also result in extra peak broadening due to their elevated viscosity. In the case of the polar surface of HPHT diamond, containing hydroxyl- and carboxyl- groups, the combination of electrostatic and hydrogen bonding interactions are expected, so the use of methanol based mobile phases could be potentially beneficial for the chromatographic use of diamond packed columns.

Due to this difference in the retention mechanism, mobile phase composition affects retention in HILIC and ANP modes in different ways. According to Hemstrom and Irgum [12], in the case of the partitioning mechanism, a direct correlation between log$k$ and concentration of the stronger eluting component has to be observed (Eq. (1)), while the surface adsorption mechanism is described by the Snyder-Soczewinski model (Eq. (2)):

$$\text{Partitioningmodel}: \log k = \log k_{org} - \mathrm{S}.\varphi_{\mathrm{w}} \quad (1)$$

$$\text{Adsorptionmodel}: \log k = \log k_w - \mathrm{A_s}/\mathrm{n_w}.\log X_w \quad (2)$$

here, k_{org} is the retention factor in 100% of the weaker mobile phase component (organic solvent), φ_w is volume fraction of the eluting species (water), S is the slope, k_w is the retention factor in the stronger component (water), X_w is molar fraction of stronger component (water), and A_S and n_w are the cross-sectional areas of the molecules of solute and water, respectively.

It has been reported that HPHT diamond stationary phases retain organic molecules in NP-HPLC through dipole–dipole and hydrogen bonding interactions [2]. Therefore, they can take place in the ANP mode as well. In contrast, the existence of a partitioning mechanism is questionable, due to the non-porous structure of HPHT diamond, which limits the formation of a stable water-enriched layer. HILIC type behaviour have been recently reported for phenols and benzoic acids retained upon a column packed with microdispersed sintered nanodiamond (MSND) [7,29,30]. However, it should be noted that the MSND surface has a more complex surface chemistry, with both positively and negatively charged groups, therefore the adsorption properties, especially those related to ion-exchange, differ substantially from those known for HPHT [31]. The aim of this work, accordingly, is to investigate the chromatographic properties of HPHT diamond in organic solvent enriched eluents, with a focus on the retention mechanism and separation selectivity at play.

2. Experimental

2.1. Instrumentation

An Accela 1250 UHPLC (Thermo Fisher Scientific, Waltham, MA, USA) was used in this work with photometric detection at 254 nm unless otherwise stated. ChromQuest™ software (Thermo Fisher Scientific, Waltham, MA, USA) was used for operating the UHPLC system and processing the chromatographic data. Retention factors for the analytes were calculated based on the peak maximum, and the void volume was determined as described in the Supplementary information. Column efficiency and peak asymmetry were calculated according to IUPAC recommendations [32] using the peak width at 10% height. The Exponentially Modified Gaussian (EMG) model was applied for the calculation of parameters for asymmetric peaks ($A_s > 1.2$) [33].

2.2. Reagents

Deionised water (DIW) was obtained from a Milli-Q (USA) system, and HPLC grade solvents 2-propanol (IPA), (Chem-Supply, Gillman, SA, Australia), acetonitrile (ACN) and methanol (MeOH) (both from Sigma-Aldrich, Castle Hill, NSW, Australia) were used for the preparation of mobile phases and solute standards. KOH, tetramethylammonium hydroxide (TMAOH), trifluoroacetic acid (TFA) (all from Sigma-Aldrich, Castle Hill, NSW, Australia), CH_3COONH_4 (Univar, Ingleburn, NSW, Australia), NH_4OH (Chem-Supply, Gillman, SA, Australia), NaCl (Ajax Chemicals, Thermo Fisher, Scoresby, VIC, Australia), formic acid (Univar, Downers Grove, IL, USA), acetic acid (BDH chemicals, Murarrie, QLD, Australia), and HCl (Merck KGaA, Darmstadt, Germany) were also used for the preparation of mobile phases. Pure solute standards for the chromatographic characterisation of HPHT diamond (Table 1) were supplied by Sigma-Aldrich (Castle Hill, NSW, Australia). All chemicals used in buffer preparation were at least >99% grade, and all solute standards were at least >98% grade. All solvents were degassed prior to use and stored in airtight containers. Aqueous solutions were handled in plastic containers, and solutions containing organic phase were stored in glass bottles and vials.

2.3. Acid-base (Boehm) titration

Acid-base potentiometric titration was accomplished using a Metrohm 809 Titrando autotitrator with Tiamo 1.2 software (MEP, Mitcham, VIC, Australia). Prior to titration, acidic groups at the surface of HPHT diamond were protonated by consecutive washing with 5 mM HCl and DIW, and dried at 100 °C. In this experiment, aqueous solutions of ~2 mM NaOH, $NaHCO_3$, Na_2CO_3 and HCl were used. NaOH was normalised by titration with potassium hydrogen phthalate (KHP), HCl was normalised with a prepared NaOH standard solution, and $NaHCO_3$ and Na_2CO_3 were normalised using HCl. The standard solution of KHP was prepared by dissolving a precisely weighed amount of anhydrous salt in water in a volumetric flask. Volumetric titration in water-organic mixtures was performed using 80% ACN – 20% DIW and 80% MeOH – 20% DIW.

The procedure for the titrations carried out in this work was based upon the original work of Boehm [34]. 1.0 g of dried HPHT diamond was placed in twelve 25 mL glass vials to make three sets of four vials. These three sets were filled with 16 mL of DIW, MeOH or ACN, respectively. 4.0 mL of previously normalised solutions of NaOH, $NaHCO_3$, Na_2CO_3 or HCl (~2 mM) were added to the vials in each set. Vials were kept for one hour, being sporadically shaken. After centrifugation, the supernatant was collected and filtered through a 0.22 μm pore size Nylon filter. Aliquots of 15 mL of filtrates were titrated with either HCl (in the case of vials containing NaOH, $NaHCO_3$, and Na_2CO_3) or NaOH (HCl containing vials)