



Study of hydration process on silica hydride surfaces by microcalorimetry and water adsorption



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ABSTRACT

A series of hydrosilated stationary phases were compared with respect to their hydrophilic–hydrophobic properties. The stationary phases were also compared to the bare silica gel used for this synthesis. The investigations were done using microcalorimetric measurements of methanol and acetonitrile heats of immersion. Because these stationary phases are used in both the reversed-phase and aqueous normal phase modes of liquid chromatography, the excess isotherm of water from acetonitrile solution was measured.

From the materials tested the highest polarity was exhibited by the silica hydride and the bare silica. The Diamond Hydride is less polar. The highest hydrophobicity is exhibited by the hydrosilated stationary phase which contains bonded octadecyl ligands.

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1. Introduction

Hydrophilic interaction liquid chromatography (HILIC) is a mode for the separation of polar compounds generally in aqueous solutions of acetonitrile, with high acetonitrile concentration [1]. For binary hydro-organic mobile phases in contact with a polar adsorbent surface, significant amounts of water are adsorbed and form a diffuse layer near the surface. This significant enrichment of water has to be considered when using aqueous solutions as the mobile phase on polar adsorbents [2]. The opposite situation is observed for the hydrophobic adsorbents used in reversed phase liquid chromatography (RPLC) where the organic modifier is preferentially adsorbed [3–7].

The water-rich layer above the surface governs the mixed retention of polar compounds under HILIC conditions. Higher organic modifier concentrations result in stronger repulsion of polar analytes from the aqueous–organic bulk mobile phase and retention volumes increase. This phenomenon leads to the ‘HILIC-half’ of the U-shape plot of the retention factor as a function of the organic modifier content in the mobile phase [8].

Silica-hydride based HPLC stationary phases were first conceived as an alternative to other types of silica materials more than 20 years ago. More recently it has been demonstrated that hydride-based stationary phases possess a broader range of

chromatographic properties that are unique when compared to other separation media [9–12]. Among the advantageous features of hydride separation materials is their ability to be used over a wide range of mobile phase compositions from 100% aqueous to pure non-polar organic solvents. As a result of this solvent versatility, the silica hydride stationary phases can function in at least three different separation domains: high water reversed-phase, high organic with some water present (aqueous normal-phase) and pure organic (organic normal-phase). The RP and aqueous normal-phase (ANP) modes are highly complementary because water is the common component in the mobile phase. With silica hydride-based stationary phases it is possible to rapidly change from RP to ANP due to the rapid equilibration of these separation materials and in some cases both mechanisms operate simultaneously, thus retaining both hydrophobic (by RP) and hydrophilic (by ANP) compounds in a single isocratic run [9]. Based on a number of studies of silica hydride-based stationary phases it is now known that the relative amount of RP and aqueous normal-phase capabilities can be adjusted by varying the surface composition [9]. The retention properties are determined by a combination of the silica hydride surface and the organic moiety attached to it. Silica hydride separation materials with a low-carbon content provide the best ANP retention capabilities for hydrophilic compounds [13,14]. As the amount of carbon bonded to the hydride surface increases, the RP retention characteristics are enhanced. The designation of ANP is used in this report to distinguish silica hydride materials that have dual retention capabilities from HILIC stationary phases which only retain polar compounds.

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The microcalorimetric measurement of the thermal effect accompanying wetting of the stationary phase by an organic solvent is a useful method that can give information about solvent interactions with the adsorbent surface [15]. It should be noted that temperature strongly influences the solvation processes [16]. It was observed that microcalorimetric measurements allow characterizing the polar properties of adsorbents. The heats of solvent immersion exhibit excellent correlation with silanol activity determined in the chromatographic system. [17]. This methodology may be used for the measurement of hydrophobic–hydrophilic properties of adsorbent surfaces.

The goal of the present study was to characterize the polar properties of hydrosilated adsorbents based on silica hydride. The microcalorimetric measurements of methanol and hexane immersion heats can be used to compare the polar properties of the adsorbent and predict the potential ability for polar interaction during chromatographic elution. Determination of water adsorption isotherms on the tested adsorbent is also a useful tool for investigating the degree of polar interactions and water adsorption of the materials. The affinity of water molecules to the adsorbent surface is an important parameter which determines the utility of a given adsorbent for HILIC and ANP chromatography.

2. Theory

The excess adsorption isotherm of a strongly adsorbed solvent from solution mixtures containing a weak solvent may be measured experimentally as a difference between the amount of the component that would be present in a hypothetical system without surface influence and the amount of component in the system with surface influence [18]. The chromatographic process on the basis of adsorption theory was described by Wang et al. [19] and Riedo and Kováts [20]. The retention volume of a component that passes through the column is a result of the mass flow rate and the mass transfer between the liquid phase and the stationary phase surface. The transport equation allows combining retention with adsorption. For binary mixtures, the universal mass balance equation may be solved analytically [21].

The excess isotherm of the adsorbed solvent from water solution per unit amount of stationary phase surface can be calculated with the following equation [22]:

$$\Gamma(C) = \frac{1}{S} \int_0^C (V_R(C) - V_M) dC \quad (1)$$

where V_R is a retention volume of the perturbation peak, V_M is the thermodynamic void volume of the column [23], S is a total surface area of the adsorbent in the column and Γ is the excess adsorption isotherm of the analyte [mol/m^2] at concentration C [mol/L].

The thermodynamic void volume of the column (V_M in Eq. (1)) is obtained by integrating the retention times of the perturbation peaks (from 0% to 100% of the organic modifier) [18]:

$$V_M = \frac{1}{C_{\max}} \int_0^{C_{\max}} V_R(C) dC \quad (2)$$

The maximum concentration of the adsorbed solvent (C_{ads}) can be found by extrapolating the slope of the excess isotherm in the linear region to the y -axis, or it can be calculated as the intercept parameter of the straight line fitted to the linear region of the excess isotherm.

The thickness of the adsorbed layer (τ) can be calculated with the following equation [24]:

$$V_{\text{ads}} = SC_{\text{ads}}v = S\tau \quad (3)$$

where v is the molar volume of the adsorbed component and V_{ads} is a volume of adsorbed solvent.

3. Experimental

3.1. Materials

Four stationary phases were tested: silica, silica hydride, Diamond Hydride and Bidentate C18. All columns were manufactured by MicroSolv Technology (Eatontown, NJ, USA). Physico-chemical characterization of adsorbents packed into stainless steel 75×4.6 mm I.D. columns are shown in Table 1.

The ^{29}Si CP/MAS NMR measurements of the bare silica gel confirm the presence of three types of silanol on the silica surface, i.e. geminal silanols ($\delta = -92$ ppm), single silanols ($\delta = -102$ ppm), and siloxane groups ($\delta = -112$ ppm). In the case of the silica hydride and the Diamond Hydride materials the signal corresponding to Si–H bonds was found at $\delta = -86$ ppm. The signal of single silanols was very low which confirms that the surface is modified and covered with Si–H groups. The structures of stationary phases are presented in Fig. 1.

The structure of Diamond Hydride is not provided. This material in addition to the Si–H bonds on the surface contain also some organic groups (2% of carbon content based on the manufacturer's information) [25]. The coverage density of the Bidentate C18 chemically bonded phase equals $2.93 \mu\text{mol}/\text{m}^2$. The ^{13}C NMR spectrum of this phase is shown in Fig. 2. It confirms the bonding of octadecyl groups to the silica surface. The number of each peak in the spectrum corresponds to the position of the atom from the silica gel surface.

Water was purified using a Milli-Q water purification system (Millipore, Bedford, MA, USA). Acetonitrile (ACN) and tetrahydrofuran (THF) for HPLC, chromatographic grade, were obtained from J.T. Baker (Deventer, The Netherlands).

3.2. Instruments

The calorimetric measurements were carried out using a homemade microcalorimeter of the Tian–Calvet isothermal type [26]. The temperature of measurement was 37°C [27,28].

A Dionex UHPLC Ultimate 3000 consisting of a binary pump, a DAD detector, and an autosampler, column thermostat and data acquisition station was used for chromatographic tests. Measurements were done at 30°C .

3.3. Methods

The study of the immersion heat was carried out using a Tian–Calvet calorimeter. Before measurement the calorimeter was calibrated. A sample of 300 mg of the stationary phase was dried at 100°C under vacuum. The silica material was placed into the microcalorimeter in a vessel and 5 cc of the solvent was added. The silica material was separated from the solvent using metal foil. After a constant temperature of the calorimeter was reached (18 h) the silica material was flooded by the solvent. The heat of the immersion was measured as changes in the temperature over the time.

Water adsorption on the tested stationary phases was done according to methodology described recently by Vajda et al. [29]. For water adsorption measurements from acetonitrile solution each column was equilibrated with a mobile phase of decreasing concentration of acetonitrile in water (100, 98, 94, 92, 90, 80, 70, 60, 50, 40, 30, 20, 10, 8, 6, 4, 2, 0) by pumping at least 20 ml of solvent mixture through the column. Perturbation of the base line was done by 2–25 μL injections of water (depending on the mobile phase composition). The signal was detected with a UV detector at $\lambda = 195$ nm. Excess adsorption isotherms were calculated based on Eqs. (1) and (2).

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