Correlations between the zeta potentials of silica hydride-based stationary phases, analyte retention behaviour and their ionic interaction descriptors

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HIGHLIGHTS

- Zeta potential measurements were used to study key silica hydride properties.
- Origin of the retention behaviour of basic, acidic and neutral analytes investigated.
- Correlation analyses of zeta potential and analyte retention established.
- Linear solvation energy relationship revealed the role of ionic contributions.
- New insights into the retention mechanisms for HILIC and ANPC modes achieved.

GRAPHICAL ABSTRACT
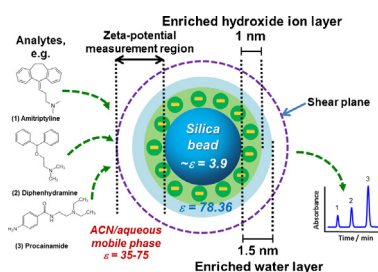
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ABSTRACT

In this study, the zeta potentials of type-B silica, bare silica hydride, the so-called Diamond Hydride[TM] and phenyl substituted silica hydride stationary phases have been measured in aqueous-organic media and correction procedures developed to account for the more negative zeta potential values in media containing different acetonitrile contents. Retention studies of 16 basic, acidic and neutral compounds were also performed with these four stationary phases with mobile phases containing 0.1% (v/v) formic acid and various acetonitrile–water compositions ranging from 0–90% (v/v) acetonitrile. The retention properties of these analytes were correlated to the corrected stationary phase zeta potentials measured under these different mobile phase conditions with R^2 values ranging from 0.01 to 1.00, depending on the stationary phase and analyte type. Using linear solvation energy relationships, stationary phase descriptors for each stationary phase have been developed for the different mobile phase conditions. Very high correlations of the zeta potentials with the ionic interaction descriptors were obtained for the type-B silica and the Diamond Hydride[TM] phases and good correlation with bare silica hydride material whilst there was no correlation observed for the phenyl substituted silica hydride phase. The nature of the retention mechanisms which gives rise to these different observations is discussed. The described methods represent a useful new approach to characterize and assess the retention properties of silica-hydride based chromatographic stationary phases of varying bonded-phase coverage and chemistries, as would be broadly applicable to other types of stationary phase used in the separation sciences.

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1. Introduction

With porous silica-based stationary phase materials, conventional end-capping techniques with trimethylsilyl (TMS) groups

Nomenclature

a	constant of linear equation
a	radius of the particle
A	parameters related to the contributions of the stationary phase to hydrogen bond acidity
ACN	acetonitrile
ANP	aqueous normal-phase
b	constant of linear equation
B	parameters related to the contributions of the stationary phase to hydrogen bond basicity
C	parameters related to the contributions of the stationary phase to ionic interaction
DH	Diamond Hydride^{TM}
e	elementary charge
EOF	electroosmotic flow
$f(\kappa a)$	Henry's function
H	parameters related to the contributions of the stationary phase to hydrophobic effects
HILIC	hydrophilic interaction chromatography
I	ionic strength
k_B	Boltzmann constant (energy)
k	retention factor (chromatography)
K	equilibrium constant of retention
K_a	acid dissociation constant
$\log k_0$	correlation factor in linear solvation energy relationship
LFER	linear free energy relationships
LSER	linear solvation energy relationships, M abbreviated parameter only used in this study, $M = -\frac{2\delta^d}{\sqrt{8\varepsilon IRT}}$
N_A	Avogadro's number
q	constant related to the charge of analytes
r	distance from the particle's centre
R	universal gas constant
S	parameters related to the contributions of the stationary phase to steric effects
T	temperature (K)
TMS	trimethylsilyl
v/v	volume by volume ratio
u_e	mobility of the particle
α'	parameters related to the contributions of the analyte to hydrogen bond basicity
β'	parameters related to the contributions of the analyte to hydrogen bond acidity
ε	dielectric constant of the medium
η	viscosity of the medium
η'	parameters related to the contributions of the analyte to hydrophobicity effects
κ	inverse Debye length
κ'	parameters related to the contributions of the analyte to ionic interaction effects
σ'	parameters related to the contributions of the analyte to steric effects
δ^d	charge on particle surface
φ	phase ratio
$\psi(a)$	Stern potential at the distance a from the particle's centre
$\psi(r)$	potential at the distance r
$\psi(a + \kappa^{-1})$ or ζ	zeta-potential at the shear plane of the particle
ΔG°	Gibbs free energy
ΔU	electrostatic potential energy

are known to provide only partial coverage of the residual silanol groups of the silica. This is mainly due to the microporosity of the stationary phase and steric hindrance of the TMS group compared to the smaller size of the adjacent free silanol groups [1]. These residual silanols often result in strong chromatographic retention, and even irreversible adsorption, of basic compounds, mainly via hydrogen bonding and ionic interactions. Collectively, these properties can lead to low analyte recovery, unsatisfactory peak shape and poor reproducibility [1–4]. To determine the levels of free silanol groups, different methods of quantitative analysis have been reported, including measurement of the electro-osmotic flow in capillary electrophoresis, the streaming potential of silica surfaces or retention time analysis of basic compounds in liquid chromatography [1].

Silica hydride stationary phases, which are based on high purity low-metal content type-B silica, were developed 10 years ago to complement conventional silica materials [5]. The fabrication of silica hydride utilizes a silanization reaction that generates a surface predominantly populated with silicon-hydride groups (Si-H), which are non-polar in nature and stable in most aqueous-organic environments. Further modification of the hydride surface through hydrosilation produces a bonded stationary phase with specific properties as a separation material with composite hydrophobic, hydrophilic and ion-exchange characteristics. Silica hydride phases have been employed in the hydrophilic interaction (HILIC) and aqueous normal phase (ANP) modes of chromatographic separation of a wide range of analytes, e.g. peptides, proteins, nucleotides and pharmaceutical compounds as well as for the separation of plant, bacterial and human metabolites [3,6–9]. Although most silanol groups on the surface of silica hydride phases can be modified by the bonded surface chemistry, strong retention of basic compounds and peptides has been observed when aqueous mobile phases have been used, even at pH values below pH 3.0, a property that has been attributed to the presence of residual silanols [10].

Hitherto, the performance of silica hydride-based stationary phases has largely been based on liquid chromatography methods relying on the resolution of a standard set of analytes. Beyond the determination of analyte retention, the identification of stationary phase descriptors using linear free energy relationships (LFERs) and linear solvation energy relationships (LSERs) has also been proposed as an additional method to aid the characterization of stationary phases [11,12]. With carefully chosen sets of standard analytes, the impact of various interactions, such as hydrogen bonding, ionic and hydrophobic interactions or pore-dependent steric effects can be identified [13] However, these methods are mobile phase and compound-set dependent and can often be time-consuming. Moreover, in common with other materials used to separate analytes in the HILIC or ANP chromatographic modes, the separation mechanism of silica-hydride stationary phases has thus yet to be fully elucidated.

Recently, the use of zeta potential measurements was suggested as an alternative method for the analysis of bare silica phases and other types of stationary phases under different mobile phase conditions with or without acidic or buffer additives present [14–16]. The zeta potential of a stationary phase material in each medium can, in principle, be measured within a few minutes using very small quantities of mobile phase containing dispersed stationary phase particles. The method is sensitive to the charge on the particle's surface, including accumulated charged species within the Debye length from the particle surface. The effects of the mobile phase composition on the ionization of functional groups or water enriched layers on the stationary phase surface can also be observed during zeta potential measurements [17–19].

Our previous studies [15,16] documented that the zeta potential values of a silica hydride phase, referred to as Diamond Hydride^{TM}