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Characterization of a novel pyridinium bromide surface confined ionic liquid stationary phase for high-performance liquid chromatography under normal phase conditions via linear solvation energy relationships

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Abstract

Utilizing linear solvation free energy relationship methodology, a novel pyridinium bromide surface confined ionic liquid (SCIL) stationary phase was characterized under normal phase high-performance liquid chromatographic conditions. A limited set of neutral aromatic probe solutes were utilized to rapidly assess the utility of the LSER model, using mobile phases of hexane modified with 2-propanol. The excellent correlation of the global fit across the mobile phase composition range used in this study for the experimental and calculated retention values ($R^2 = 0.994$) indicates that the LSER model is an appropriate model of characterizing this polar bonded phase under normal phase conditions. For a limited subset of compounds, retention on the pyridinium bromide SCIL stationary phase is more highly correlated with that obtained on a cyano column than on a diol column under NP conditions.
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1. Introduction

The distinct merits of reversed phase (RP) high-performance liquid chromatography (HPLC) (e.g., broad applicability, general robustness) position it as the dominant mode of liquid chromatography. The introduction of new reversed phase media reinforces this dominance [1]. Recently, stationary phases containing covalently bound surface confined ionic liquid (SCIL) groups have been reported in the literature [2–6]. Their ability to separate individual classes of compounds under reversed phase conditions, and the physical characterization of these SCIL phases have been the primary focus of these reports [3].

Although a significant hurdle to widespread application of normal phase chromatography resides in reproducibility issues arising from energetically inhomogenous surfaces [7], bonded ligands such as aminopropyl [8,9] or cyano [10] provide potential electron donor/acceptor, dipole–dipole or hydrogen bonding interactions available under normal phase conditions that may offer advantages for the separation of polar analytes due to significant intermolecular interactions with the polar stationary phase [7]. Hence, the retention mechanism of the SCIL phase under normal phase conditions is of interest. In this work, the retention mechanism of a novel pyridinium bromide stationary phase is investigated using linear solvation energy relationships (LSER) under normal phase conditions.

LSER have been used extensively to elucidate retention mechanisms in reversed phase liquid chromatography [2,3,11,12]. In contrast, LSER-based characterization of normal phase chromatography is far less common. The LSER methodology [13–15], relating retention of an analyte on a stationary phase ($\log k$) to a linear relationship of fundamental solute descriptors (Abraham's solute descriptors) [11], usually takes the form of

$$\log k = rR_2 + s\pi_2^* + b\sum \beta_2^{\mathrm{H}} + a\sum \alpha_2^{\mathrm{H}} + vV_2 + \log k_{\mathrm{o}} \quad (1)$$

Recently, a different nomenclature has been adopted for the solute descriptors to simplify the model expressions [12,16,17], where the revised LSER equation takes the form of

$$\log k = e\mathbf{E} + s\mathbf{S} + b\mathbf{B} + a\mathbf{A} + v\mathbf{V} + \log k_{\mathrm{o}} \quad (2)$$

Specifically, R_2 or $\mathbf{E}$ represent the excess molar refraction, which reflects polarizability contributions from π- and *n*-electrons; π_2^* or $\mathbf{S}$ are the solute dipolarity/polarizability; $\sum \alpha_2^{\mathrm{H}}$ or $\mathbf{A}$

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and $\sum \beta_2^H$ or **B** are the overall solute hydrogen bond acidity and basicity, respectively, which scale as the hydrogen bonding propensity of a solute to surrounding solvent molecules; V_2 or **V** are McGowan's characteristic volume. The $\log k_o$ term is thought to include the phase ratio of the chromatographic system [2,3]. It should be noted that both of the stated models, Eqs. (1) and (2), fundamentally describe retention based upon global free energy principles directly related to the intermolecular interactions that occur between an analyte and the stationary/mobile phase system.

In the LSER equations, the coefficients (*e*, *s*, *b*, *a*, *v* and $\log k_o$), extracted from multiple linear regression analysis of the retention data, represent the difference of a specific interaction of the solutes between the stationary and mobile phases [18,19]. Overall, both the sign and the magnitude of the coefficients are critical in assessing whether the stationary or the mobile phase displays the greater interaction with the solute via a specific interaction mode.

While used extensively in gas chromatography and reversed phase HPLC [11,12], the application of the LSER method to normal phase HPLC [8,13–15,20,21] has been somewhat sparse, perhaps because of the more limited application range of normal phase HPLC relative to gas chromatography and reversed phase HPLC. Furthermore, because the retention mechanism of silica phases is based on adsorption, the LSER model, which is based on the cavity model of salvation [11], may not be entirely appropriate. Indeed, normal phase LSER studies on silica phases have shown reduced correlations [20–22] relative to reversed phase characterization. However, LSER has been somewhat successful at modeling normal phase retention on polar bonded phases [22].

As mentioned above, it should also be noted that interpretation of the terms extracted from the LSER equation are highly dependent on the mode of chromatography utilized. For instance, in reversed phase chromatography, the *v***V** term is loosely related to the hydrophobicity of the stationary phase [2,3]. However, in normal phase studies, in the absence of water, the *v***V** accounts for the ability of the mobile phase to participate in dispersive interactions and the relative energy required to form a "hole" in either the mobile phase or the stationary phase for the analyte [18].

In the present work, normal phase LSER studies were performed on a pyridinium bromide-modified stationary phase, using a limited set of neutral aromatic probe solutes (Table 1). The limited set of solutes was used to rapidly assess the utility in characterizing the pyridinium bromide SCIL phase under normal phase conditions [23].

Table 1
Solvation solute descriptors for the probe solutes

Probe solute	Descriptors				
	E	**S**	**A**	**B**	**V**
Benzene	0.610	0.52	0.00	0.14	0.716
Anthracene	2.290	1.34	0.00	0.26	1.454
Toluene	0.601	0.52	0.00	0.14	0.857
Mesitylene	0.649	0.52	0.00	0.20	1.139
Ethylbenzene	0.613	0.51	0.00	0.15	0.998
Propylbenzene	0.599	0.50	0.00	0.15	1.139
Chlorobenzene	0.718	0.65	0.00	0.07	0.839
Phenol	0.805	0.89	0.60	0.30	0.775
Benzyl alcohol	0.803	0.87	0.33	0.56	0.916
2-Phenyl ethanol	0.811	0.91	0.30	0.64	1.057
p-Cresol	0.820	0.87	0.57	0.31	0.916
p-Chlorophenol	0.915	1.08	0.67	0.20	0.898
Nitrobenzene	0.871	1.11	0.00	0.28	0.891
Benzonitrile	0.742	1.11	0.00	0.33	0.871
Benzaldehyde	0.820	1.00	0.00	0.39	0.873
Anisole	0.708	0.75	0.00	0.29	0.916
Fluorobenzene	0.477	0.57	0.00	0.10	0.734
Acetophenone	0.818	1.01	0.00	0.48	1.014
p-Xylene	0.613	0.52	0.00	0.17	0.998
o-Xylene	0.663	0.56	0.00	0.16	0.998
1-Napthol	1.520	1.05	0.61	0.37	1.144
Biphenyl	1.360	0.99	0.00	0.22	1.324
Bromobenzene	0.882	0.73	0.00	0.09	0.891

2. Experimental

2.1. Materials

For the NP studies, a set of 23 neutral aromatic probes solutes (Table 1), with low cross-correlation in their molecular descriptors (Table 2), were selected [2,13]. Mobile phase components (HPLC-grade water, 99% pure HPLC-grade hexane, heptane, and methanol) were supplied by Tedia (Fairfield, OH); 2-propanol was supplied by Pharmco (Brookfield, CT). Most probe solutes were purchased from either Sigma–Aldrich Corp. (St. Louis, MO) or Fisher Scientific Chemical Co. (Pittsburgh, PA). Anthracene was purchased from Eastman Organic Chemicals (Kingsport, TN), mesitylene from J.T. Baker Chemical Company, (Phillipsburgh, NJ), 2-phenylethanol from ICN Biomedicals (Irvine, CA), benzonitrile, biphenyl, and anisole from Acros Organics (Morris Plains, NJ).

All reagents used in the synthesis of the stationary phase; hexachloroplatinic(IV) acid hydrate, 8-bromo-1-octene, trichlorosilane, chlorotrimethylsilane, pyridine, anhydrous toluene, 2,6-lutidine; were purchased from the Sigma–Aldrich Corp. (St. Louis, MO). The silica sorbent was a spherical 5 μm, 100 Å pore Symmetry® silica provided by the Waters Corporation (Milford, MA).

2.2. Methods

2.2.1. Stationary phase synthesis

The pyridinium bromide-modified silica phase was prepared by hydrosilyation of the alkenylbromide followed by immobi-

Table 2
Correlation coefficient matrix of solute descriptors

	E	**S**	**A**	**B**	**V**
E	1	0.722	0.173	0.186	0.186
S		1	0.346	0.538	0.340
A			1	0.363	−0.093
B				1	0.146
V					1

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