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Characterization of surface confined ionic liquid stationary phases: Impact of cation revisited

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ABSTRACT

Modification of the Linear Solvation Energy Relationship (LSER) equation to account for ionic interactions in the retention of ionizable compounds has enabled the elucidation in the effect of the imidazolium cation identity on retention. Three Surface Confined Ionic Liquid stationary phases were synthesized from an octylbromide phase on silica: 1-octyl-3-methylimidazolium bromide (MIM), 1-octyl-3-butylimidazolium bromide (BIM), and 1-octyl-3-benzylimidazolium bromide (BzIM). These phases were probed via a 35 analyte probe set, including 6 phenolic acids, 5 anilinic bases, and 2 pyridinic bases, and the resulting column parameters compared with previously reported interactions of ionic liquids or Surface Confined Ionic Liquids. The correlation between experimental and calculated retention for the conventional, 6-parameter LSER equation was very poor: $r^2 = 0.64$ (MIM), 0.60 (BIM), and 0.62 (BzIM). By accounting for the ionic interactions between stationary phase and analytes, linearity for the modified, 8 parameter LSER equation was significantly improved to $r^2 = 0.997$ (MIM), 0.996 (BIM), and 0.997 (BzIM). The primary difference between cation identities is within the retention of acids where BIM > BzIM > MIM. We conjecture that the accessibility of bulky, acidic analytes to the on-top interaction of the imidazolium ring is the major contributor to increased anion retention.

1. Introduction

Ionic liquids (IL) are salts that flow at practically low temperatures. They tend to have a carbon chain terminated in an ionized moiety associated with a counter-ion, allowing for multiple intermolecular interactions that can be tuned by changing the length of the carbon chain, the identity of the ionized group, and the identity of the counter-ion. Ionic liquids as mobile phase additives in liquid chromatography allow for tunable interactions between the analytes and the stationary phase with the goal of improving the separation of ionized compounds [1]. However, the IL additives are incompatible with mass spectrometry and evaporative light scattering and increase the background signal for UV absorbance detectors.

Surface Confined Ionic Liquids (SCIL) are chromatographic stationary phases that arise from bonding an IL to the sorbent support. These stationary phases are inherently multi-modal, exhibiting reversed-phase retention via the long carbon chains and ion-exchange retention via the ionized moiety [1]. Imidazolium based ionic liquids act as strong anion-exchange media and can be modified with different N-alkyl groups to alter the chromatographic selectivity of the phase [2,3]. Pino and Alfonso recently published an excellent review of SCIL phases in reference [4].

Chromatographic retention can be modeled by a sum of intermolecular interactions via the conventional Linear Solvation Energy Relationship (LSER) model:

$$\log k' = eE + sS + aA + bB + vV + \log k'_0 \qquad (1)$$

where k' is the retention factor, k'_0 is a system constant, the capital letters (E, S, A, B, V) are solute descriptors measured and reported by Abraham [5] for analytes used to probe the system, and the lower case letters (e, s, a, b, v) are the system descriptors for the column. Descriptor pairs eE, sS, aA, bB, and vV describe the influence of excess polarizability, polarizability/dipolarity, hydrogen bond donating ability, hydrogen bond accepting ability, and molecular size, respectively, on the retention of individual analytes in a given column. Direct comparison of columns' retention under a given set of conditions are possible by comparing the magnitude of e, s, a, b, and v [6].

Previous work by the Stalcup group [7] characterized the impact of the cation identity of imidazolium phases via the 6-parameter LSER model (hereafter called the conventional model). However, this earlier work did not include a suitable number of weak bases or weak acids in the probe solute set to adequately interact with

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the immobilized cations. The main conclusion for the identity of the cation was that the correlation between log k' plots of the methylimidazolium, butylimidazolium, and benzylimidazolium phases indicated that the cation does not change the energetics of retention significantly. However, Fields et al. later showed that if more weak acids were added into the probe solute set using the 6 parameter set, the LSER coefficient of correlation (r^2) would drop significantly as the model does not adequately describe the intermolecular interaction of ionized acids with the stationary phase. The first attempt to improve the LSER equation to account for ionic interaction was Abraham's j^+J^+ and j^-J^- terms [8], values solved from the fit of the 5 other parameters (E, S, A, B, and log k'_0).

Fields et al. [9] and Chirita et al. [10] modified equation 1 to include the influence of ionization to retention by including two additional, measurable descriptors [9]:

$$\log k' = eE + sS + aA + bB + vV + d^-D^- + d^+D^+ + \log k'_0 \quad (2)$$

D^- (acids) and D^+ (bases) are the percent ionized of the test analytes and d^- and d^+ are the system descriptors for the column. The descriptor pairs then describe the influence of ionization on the retention of individual analytes in a given column. It should be noted that in the previous articles, the fraction ionized was used as the definition of D rather than the percent ionized used in this work. Hereafter, Eq. (2) is referred to as the modified model. For cationic stationary phases, d^- is expected to be large and positive compared to conventional hydrophobic stationary phases. To determine the D^- or D^+ descriptor for a monoprotic analyte of a given pK_a in an aqueous solvent of a measured pH and temperature:

$$D^m = \frac{100\%}{1 + 10^{m(pH - pKa)}} \quad (3)$$

where m is – or + for a monoprotic acid or base, respectively. D^m is therefore a value between 0 and 100%. In a hydroorganic solvent, the pK_a will shift and can be calculated for different phenols [11] and other compounds [12] at 25 °C. The pH measured by a glass electrode calibrated with aqueous standards can be adjusted for the methanol (MeOH) content [13] at 25 °C. For 60% MeOH, the measured pH is increased by 0.17 units.

Alternatively, flow injection analysis (FIA) with UV spectroscopy [14] can be used to measure the percent ionization directly if there is a change in molar absorptivity between neutral and ionized forms of an analyte. Absorbance values within the hydroorganic carrier at a set temperature, pressure, and wavelength are measured at low pH (Abs_{acid}), high pH (Abs_{base}), and in an equivalent ionic strength salt-containing carrier (Abs_{salt}). The percent ionized is then calculated for acidic and basic analytes by Eqs. (4) and (5), respectively:

$$D^- = 100\,\%\, X \frac{Abs_{acid} - Abs_{salt}}{Abs_{acid} - Abs_{base}} \quad (4)$$

$$D^+ = 100\,\%\, X \frac{Abs_{base} - Abs_{salt}}{Abs_{base} - Abs_{acid}} \quad (5)$$

This FIA method is of great utility because the conditions within the spectrometer can be selected to mimic the conditions within the chromatographic column, concerning temperature, analyte concentration, system pressure, and solvent composition. The FIA method must use a strong acid, strong base, and a salt to measure the percent ionized and therefore cannot match the ionic strength of a hydroorganic mobile phase without salt added.

In this work, we report the impact of the SCIL cation on the retention mechanism by use of the modified, 8-parameter LSER model. The 35 analytes used in this study were selected to provide a range of molecular descriptor values to probe the unique separation space afforded by these novel stationary phases. As the impact of organic modifier on retention has been extensively studied in previous work [7,9], the focus of the present study was on the role of the cation and electrostatic interactions in retention. Hence, only a single hydroorganic composition was used but the impact of ionic strength was also investigated. We demonstrate that the improved the model combined with the inclusion of additional weak acids and weak bases in the probe set provides a more complete description of retention on these novel phases than obtained in the original study [7].

2. Experimental

2.1. Reagents

All water used was purified to a resistance of approximately 18 MΩ-cm. HPLC grade methanol (MeOH) was obtained from Avantor Materials (Norway). The 35 LSER test solutes, trichlorosilane, hexachloroplatinic acid, trimethylchlorosilane, and imidazole reagents were obtained from Sigma–Aldrich (St. Louis, MO, USA). Bulk toluene was dried via dean-stark trap and stored in an argon pressurized glass cylinder. Bulk tetrahydrofuran (THF) was still-dried over sodium with benzophenone indicator. The 8-bromo-1-octene was purchased from Fluorochem (Derbyshire, UK). LSER analytes were dissolved in 60% MeOH:40% H_2O by volume measured via analytical balance. Analyte concentrations were a static 1.0 mg/mL.

2.2. Instrumentation

All chromatographic studies were performed using a Shimadzu LC-20 stack (Kyoto, Japan), LC-20AD gradient pump outfitted with a DGU-20A_5 inline degasser, an SIL-20A_{HT} auto injector, a CTO-30A column oven, a SPD-M30A diode array detector, and a CBM-20A system controller. All data were collected and analyzed using Shimadzu LabSolutions Lite software. FIA experiments to determine analyte percent ionization were performed on the Shimadzu LC-20 with the column replaced with 1.3 mL of 0.025" i.d. tubing coiled within the column oven.

2.3. Columns

The imidazolium phases were all prepared in-house. All glassware used was vacuum dried at 125 °C and 200 mbar overnight then assembled quickly and purged with dry nitrogen. Glassware was presilanized with 5% trimethylchlorosilane in dry toluene prior to chlorosilane reactions. 8-bromooctyltrichlorosilane reagent was prepared by silylation of 8-bromo-1-octene with a 5:1 molar excess of trichlorosilane in 100 mL dry tetrahydrofuran in the presence of hexachloroplatinic acid hexahydrate at ~23 °C. After distillation removal of THF, the product 8-bromooctyltrichlorosilane was vacuum distilled and verified via GC-MS isotope peak height ratios to contain one component of a bromoalkyltrichlorosilane.

Derivatization of 12.5 g of 5 μm, type B Waters Symmetry silica with 8-bromooctyltrichlorosilane in refluxing dry toluene proceeded via oligomeric synthesis [15] with two serial reactions to increase ligand loading (Table 1). Reaction was completed under dry N_2 for 4 h with ~20 μL/min dropwise addition of 3.5 mL of 2,6-lutidine. Between each step of the oligomeric synthesis the silica was isolated via vacuum filtration and serially washed with 250 mL of toluene, 250 mL of MeOH, 250 mL of 50% aqueous MeOH, then 250 mL of MeOH. Post-derivatization endcapping was performed via 5% trimethylchlorosilane in dry toluene for 1 h.

Octylbromide (C_8Br) derivatized silica was segmented into four aliquots. The first aliquot of C_8Br was used as an additional control reaction (without imidazole reagent) and slurry packed into a column (Bromo). The second, third, and fourth aliquots were reacted with 3:1 molar excess methyl-, butyl-, or benzyl- imidazole reagents in 75 mL of refluxing dry toluene for 4 h to produce