Electrochemically modulated liquid chromatography: Theoretical investigations and applications from the perspectives of chromatography and interfacial electrochemistry

by

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ABSTRACT

Electrochemically modulated liquid chromatography (EMLC) employs a conductive material as both a stationary phase for chromatographic separations and as a working electrode for performing electrochemistry experiments. This dual functionality gives EMLC the capacity to manipulate chromatographic separations by changing the potential applied (E_{app}) to the stationary phase with respect to an external reference. The ability to monitor retention as a function of E_{app} provides a means to chromatographically monitor electrosorption processes at solid-liquid interfaces. In this dissertation, the retention mechanism for EMLC is examined from the perspective of electrical double layer theory and interfacial thermodynamics.

From the chromatographic data, it is possible to determine the interfacial excess (Γ) of a solute and changes in interfacial tension ($d\gamma$) as a function of both E_{app} and the supporting electrolyte concentration. Taken together, these two experimentally manipulated parameters can be examined within the context of the Gibbs adsorption equation to delineate the contribution of a variety of interfacial properties, including the charge of solute on the stationary phase and the potential of zero charge (PZC), to the mechanism behind EMLC-based retention.

The chromatographic probing of interfacial phenomena is complemented by electroanalytical experiments that exploit the ability to monitor the electronic current flowing through an EMLC column. Cyclic voltammetry and chronoamperometry of an EMLC column are used to determine the electronic performance characteristics of an EMLC column. An electrochemical flow injection analysis of a column is provided in which the current required to maintain a constant E_{app} is monitored and provides a way to examine the influence that acetonitrile and supporting electrolyte composition, flow rate, column backpressure, and ionic strength have on the structure of electrified interfaces.

CHAPTER 1. GENERAL INTRODUCTION

DISSERTATION ORGANIZATION

From the electrochemically driven flow observed in electrophoresis and electrochromatography to the use of electrochemical detectors for chromatographic analysis, the blending of electrochemistry with the separations sciences has proven highly successful. The ability of these hybrid techniques to solve complex problems has been made possible through pioneering research, during which the fundamental understanding of the underlying mechanisms at work in each system was advanced. This dissertation examines some of the fundamental properties of an electrochemically-based separation technique that combines the concepts of thin-layer electrochemistry and liquid chromatography by using an electrically conductive material as an electrosorptive stationary phase.

This section begins with background information that discusses the design development of this technique, Electrochemically Modulated Liquid Chromatography (EMLC). Once the general design and performance of EMLC has been presented, the focus will turn to a microscopic and spectroscopic overview of the carbonaceous stationary phases typically employed in EMLC. This overview will conclude with some background information on retention mechanisms on these carbon particles in EMLC and the development of Electrical Double Layer (EDL) theory to model potential dependent adsorption.

The first two chapters investigate fundamental aspects of EMLC from two different perspectives: chromatographic and thermodynamic. Both chapters study the influence of supporting electrolyte concentration and identity on the analyte in EMLC-based retention.

The first chapter uses EDL theory to describe retention in EMLC, and builds upon the current description of retention in EMLC. The second chapter looks at the electrochemical importance of these data through the use of the Gibbs adsorption isotherm.

Chapter 3 and 4 take advantage of the electroanalytical aspect of EMLC. In Chapter 3, an EMLC column is analyzed using cyclic voltammetry and chronoamperometry in determining the capacitance, equivalent series resistance, and time constant for an EMLC column. Furthermore, the potential at the auxiliary electrode is monitored in order to determine if the design of an EMLC column is limiting performance. In chapter 4, an EMLC column is employed as an electrochemical flow through cell. Instead of monitoring the current passing through an EMLC column resulting from a change in applied potential, the current is monitored as a function of changes in mobile phase composition and sample injection.

This work marks the beginnings of fundamental studies geared toward obtaining a better understanding of the interactions taking place at electrified interfaces. The retention of an analyte results from numerous interactions with the stationary phase, providing a way to determine macroscopic properties such as the free energy of adsorption and the potential of zero charge. These macroscopic properties serve as a basis for comparisons with other research in our laboratory focused on microscopic studies of electrified interfaces. These microscopic studies monitor adsorption as a function of potential using force-displacement curves obtained by atomic force microscopy or, alternatively, via spectrophotometric detection of adsorbed analyte at an optically transparent electrode.

BACKGROUND INFORMATION

Design and Development of EMLC

High performance liquid chromatography (HPLC) is one of the most important techniques in the analytical sciences.[1] Through the interplay of analyte interactions with mobile and stationary phases, HPLC is capable of separating innumerable complex mixtures. Separations of different categories of analytes, however, typically require compositionally different stationary phases. For example, reversed phase silica packings can be used to separate aromatic compounds, but a cationic packing is more useful for separations of inorganic anions. Separations can also be manipulated by changes in mobile phase composition, such as with gradient elution strategies, to enhance resolution and decrease elution time. Recently the advantages of performing EMLC separations at elevated operational temperatures have also been demonstrated.

Electrochemically modulated liquid chromatography (EMLC) is a hybrid technique that combines aspects of electrochemistry with HPLC. This merger is accomplished by using a conductive stationary phase (e.g., glassy carbon (GC) or porous graphitic carbon (PGC)) as the working electrode in a three-electrode electrochemical cell that is also configured as a HPLC column. Changes in the potential applied (E_{app}) to the working-electrode/stationary phase is envisioned to electrochemically alter the architecture of the interface, yielding the ability to manipulate the efficiency of a separation. The capability to electrochemically alter the stationary phase is similar and complementary to the use of mobile phase gradients in classical liquid chromatography for optimizing separations.

The use of an electrochemically modulated stationary phase in liquid chromatography was first reported by Fujinaga *et al.* in 1963,[2] then by Blaedel and Strohl[3] and independently by Roe[4] in 1964. While innovative, the performance of these early devices provided poor chromatographic efficiencies (10-200 plates m^{-1}). Similar to the added efficiency provided by HPLC columns over low-pressure chromatography columns, Yacynych[5] and later Wallace[6] re-engineered these early column designs to permit pressures up to 3000 psi. Even though these redesigned columns provided an improvement in chromatographic performance, the separation efficiencies (~1000 plates m^{-1}) were still low compared to typical HPLC columns.[7]

The low efficiencies observed for these early column designs demonstrate the difficulty in designing an apparatus that satisfies the performance requirements for both HPLC and electrochemistry. In HPLC, a large surface area to dead volume ratio is necessary to provide a large column capacity, and to minimize diffusion and band broadening effects in performing high-resolution chromatographic separations.[8] In electrochemistry, a small surface area to bulk solvent volume ratio is desired to decrease solution resistance and to minimize the background current that is commonly observed at heterogeneous solid electrode surfaces. In compromising these contrasting requirements, Deinhammer, Ting, and Porter introduced a two-electrode[9] and subsequently a three-electrode[10] EMLC column design with efficiencies (*e.g.*, 20,000 plates m^{-1}) much closer to those for conventional HPLC columns.

A schematic representation of the columns designed by Deinhammer *et al.* is provided in Figure 1. In constructing an EMLC column, the conductive stationary phase is slurry-packed into a porous stainless steel column that has been lined with a tubular Nafion™ membrane. The porous stainless steel column provides structural integrity for the Nafion™ tubing and performs the duty of the auxiliary electrode. The Nafion™ tube is fabricated from a copolymer of tetrafluoroethylene and perfluorinated monomers containing sulfonic

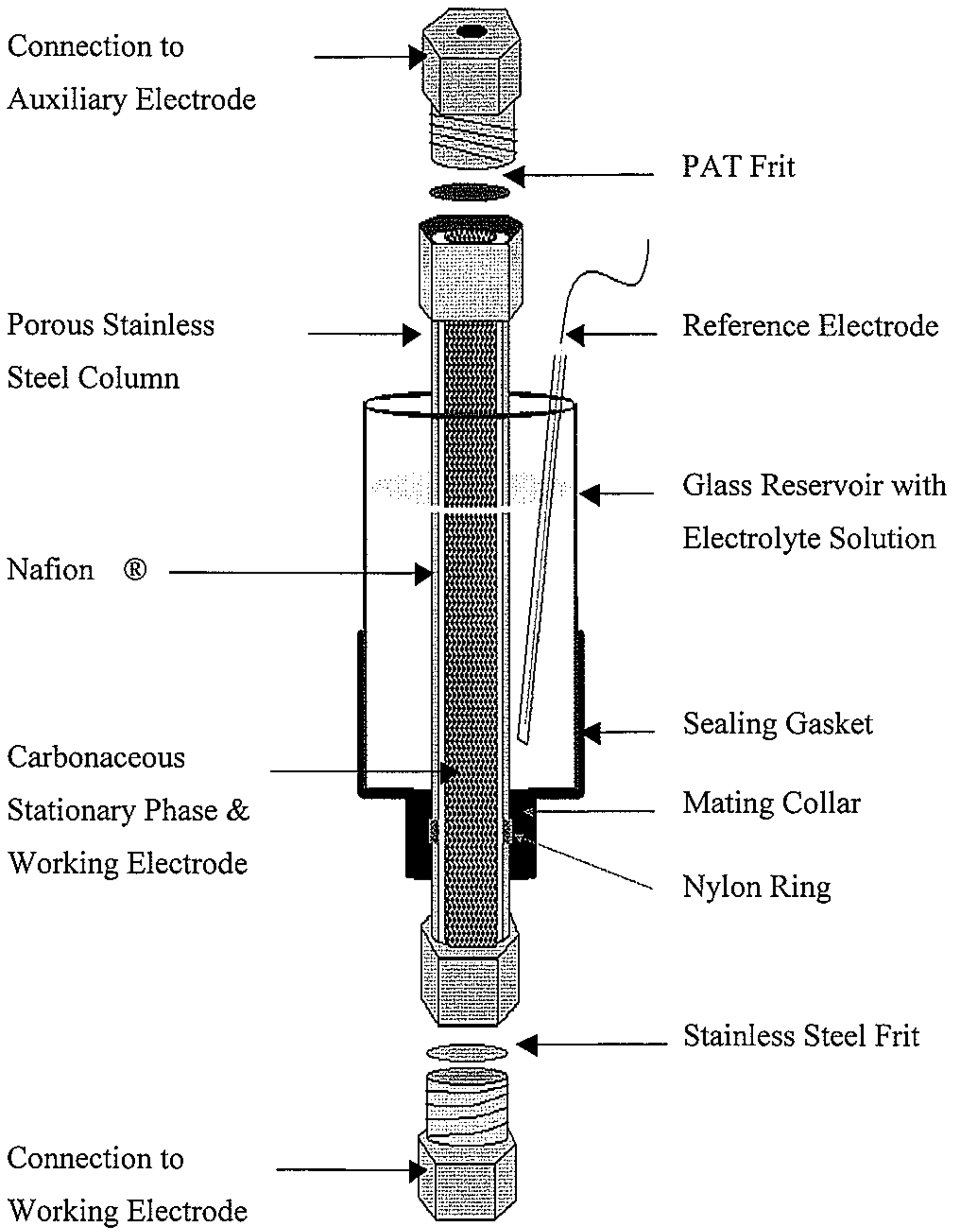

Fig. 1. *Schematic representation of the EMLC column as described by Porter and Ting.*[10]

acid groups. The resulting tube is a polymeric cation-exchange membrane that serves three main purposes: it acts as a container for the stationary and mobile phases, it electronically insulates the stationary phase from the auxiliary electrode, and it serves as a salt bridge between the mobile phase and the electrolyte reservoir. The working electrode is usually referenced to a Ag/AgCl saturated NaCl reference electrode placed in the electrolyte reservoir. The electrical connection to the stationary phase is made at the bottom of the column, where a standard HPLC column end-fitting is used in conjunction with a stainless steel frit. The bottom of the column is electrically isolated from the porous auxiliary electrode by a nylon ring that is inserted inside the PEEK union used to connect the top and bottom of the column. At the top of the column, a non-conductive PAT® (PEEK alloyed with teflon) frit insulates the working electrode from the stainless steel end-fittings that are used for the connection to the auxiliary electrode.

The difficulty in constructing an efficient EMLC column delayed extensive research on its development. Nevertheless, a variety of uses for EMLC were demonstrated. Obviously, the primary uses for EMLC columns are in the realm of HPLC type separations,[11] although other applications that employ EMLC columns have also been shown. In the early literature, the desalination and the removal of heavy metals from water examined the ability for EMLC columns to act as a rechargeable solid phase extractor.[3, 4, 12-14] A few reports also described the ability to perform on-column electrochemical reactions, as well as usage similar to packed bed electrochemical reactor. Modern EMLC columns have been applied to the separation of a wide range of compounds, including mixtures of aromatic sulfonates,[9, 10, 15] monosubstituted benzenes,[16] organic cations,[17] dansylated amino acids,[18] corticosteroids,[19, 20] benzodiazepines,[21, 22] and the enantiomers of hexabarbital and mephenytoin.[23]

History, development, and properties of EMLC stationary phases

As previously mentioned, EMLC employs electrically conductive stationary phases in order to modulate retention through the use of an externally applied electrical potential. Not only must the material be conductive, but the stationary phase must also satisfy the requirements of modern liquid chromatography.[24, 25] The stationary phase should therefore be composed of small monodisperse particles (3-10 μm) with a narrow pore size distribution that are inert, have uniform surface homogeneity, adequate mechanical strength, and can be easily manufactured with sufficient surface area in order to obtain high separation efficiencies.[26, 27] Stationary phases in EMLC have included a variety of materials from metal and metal coated glass particles to graphitic particles and to carbonaceous materials that have been coated with conducting polymeric stationary phases or covalently modified through electrosynthetic means.[5, 28-33]

Unmodified carbonaceous stationary phases constitute the most extensively used conductive stationary phase in EMLC today, which is not surprising with the long history of carbon-based materials in both the chromatographic and the electrochemical sciences. The role of carbon in electrochemistry is vast, with beginnings in the 1790's when Alessandro Volta reported that charcoal was an electrical conductor, and shortly thereafter in the work of Sir Humphrey Davy in the early 1800's on electrolysis and the production of the first electric arc. [34, 35] Since these early works, the primary electrochemical use of carbon has been as an electrode material in batteries, fuel cells, electrosynthesis, electrochemical sensors, and in double layer capacitors. More recently, however, the application of carbon nanotubes as transistors in chip-scale integrated circuits has further diversified the function of carbon in electrochemistry.[36] The employment of carbon in the separation sciences goes even further back in history, where carbon was used for filtering water in ancient India, and as an adsorbent material for medicinal purification in Egypt.[37, 38] In more modern times, the use of carbon as a chromatographic support was popular in the gas chromatography literature of the first half of the twentieth century.[39, 40]

The use of carbon as a support material for liquid chromatography started in the 1940's in which charcoal was used in the frontal and displacement chromatography of a number of small solutes.[41-43] The first specific use of carbon as a stationary phase in HPLC was reported by Kiselev,[44, 45] who used silica gel particles coated with pyrolytic carbon, and shortly thereafter by Guiochon and coworkers who employed carbon black particles.[46-48] Since these early works, a variety of methods have been established for the preparation of carbon-based HPLC stationary phases, a majority of which have been summarized in the review by Leboda et al.[49] It should be noted, however, that several more versions of carbonaceous LC stationary phases have been reported since the printing of Leboda's review, such as carbon-coated zirconia and graphitized carbon monoliths. [50, 51]

For use in EMLC, the carbonaceous stationary phases must be of sufficient electrical conductivity both across and between particles, which may limit the use of stationary phases that employ thin carbon coatings in EMLC. The first application of an electrical potential to a carbonaceous stationary phase was performed in 1964 using crushed graphite particles as the packing material.[12] Currently, the two most prevalent types of carbon particles that are employed as stationary phases in EMLC are porous graphitic carbon (PGC), which is a commercially available stationary phase marketed as Hypercarb™ (ThermoHypersil, Bellefonte, PA, USA) and spherical glassy carbon powders (GC, also known as vitreous carbon), which are more commonly used by the electrochemical industry. PGC was developed by Knox in the middle 1980's in an effort to make a carbonaceous stationary phase with similar efficiencies as other reversed phase media.[52] Briefly, PGC is produced by soaking 5-μm silica beads in a phenol-formaldehyde mixture; the soaked beads are then subjected to a temperature of 900°C. A base is subsequently added to dissolve the silica so that only the carbon network remains, and finally the carbon beads are heated to temperatures in excess of 2200°C to form the final product. The preparation of glassy carbon particles follows that of PGC, the exception being the absence of silica beads which are used to control the size and porosity of PGC. As a result, GC particles are more polydisperse and of lower surface area than PGC.

The scientific literature is full of information on carbonaceous materials, summaries of which are embodied in a select handful of useful reviews.[53-58] These reviews provide insights into the physical, chemical and electrochemical properties of a variety of carbon materials, including the GC particles often employed as EMLC absorbents. While many properties of PGC were optimized in its development to produce an efficient HPLC stationary phase,[27, 52, 59-61] PGC shares many traits with the carbonaceous materials in the above reviews. The following paragraphs employ this and other available literature to interpret and compare the structure and composition of GC with PGC stationary phases prior to discussing the mechanisms thought to govern adsorption onto these particles in an EMLC column.

Images of the carbonaceous particles taken at 5910x magnification using a Philips Model CM30 transmission electron microscope (TEM) are provided in Figure 2. In preparing these micrographs, the PGC particles (5 μm hypercarb™, ThermoHypersil, Bellefonte, PA, USA) and the GC particles (0.4-12 μm glassy carbon spherical powder, type

I, Alfa Aesar, Ward Hill, MA, USA) were crushed to enhance electron transmittance. The particles were then suspended in a solution of methanol and a small sample was pipetted onto the TEM grid for imaging. The electron beam was accelerated using a potential of 300 kV for all micrographs presented. The images on the left in Figure 2 are negatives that were digitized using a transmission scanner at 600 dpi, while the brightfield images on the right were produced from these negatives using Adobe Photodeluxe™ software.

As the images in Figure 2 illustrate, significant differences exist in the structure of the two carbonaceous stationary phases. The most striking difference is the sponge-like appearance of PGC versus the smooth appearance of the GC particles. This observation is consistent with BET (Brunauer, Emitt, and Teller) studies that indicate a surface area of 120 m^2/g for PGC versus 2 m^2/g for GC, and with the chromatographic data that show higher retention on PGC as opposed to GC.[15, 61] Another obvious difference between PGC and GC is in the size-distribution of the particles. The PGC particles are mono-disperse whereas the GC have a larger distribution of particle size, but are on average smaller than the PGC particles.

Upon inspection at higher magnification (20,000x), the images in Figure 3 show that PGC is composed of small 'ribbons' that are interwoven to form the particles. The depth of field at the high magnification is limited, but the dimensions of these ribbons can be roughly estimated at tens of nanometers thick and hundreds of nanometer in length. These dimensions were measured by zooming in on several regions of the image and physically measuring the size of the strands with photographic software. The high porosity of PGC particles is also apparent in the pictures in Figure 3, especially near the edges where the particles are thinner, and the evidence derived from these images is consistent with the manufacturer's claim of 80% porosity.

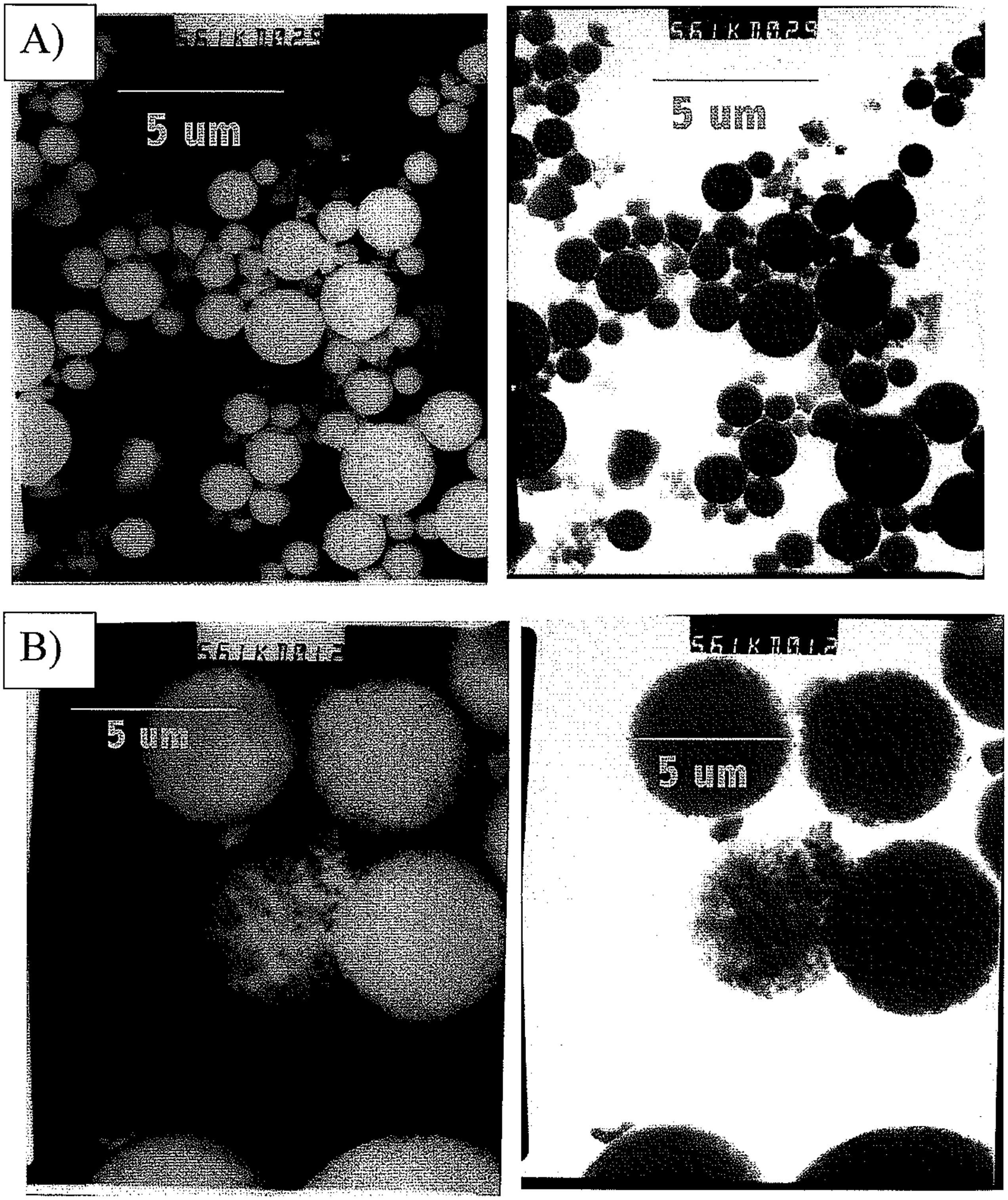

Figure 2. *Images of PGC and GC at the same magnification (5610x). A) Darkfield (left) and Brightfield (right) of GC. B) Darkfield (left) and Brightfield (right) image of PGC.*

Figure 4 shows a closer view of a crushed GC particle. First note the smooth appearance demonstrated by the bulk of the GC particle. Then notice that small inconsistencies are present within the particle which gives rise to regions of higher contrast (i.e. the dark blotches in the brightfield image). These inconsistencies vary greatly in size, and images at different magnifications show these regions to range between 35-400 nm in diameter. The source of these regions of higher contrast will be confirmed through electron diffraction to consist primarily of regions of ordered graphite.

In studying the structure of PGC and GC particles, selected area electron diffraction (SAED) was performed to determine whether the material was more or less crystalline in nature and to compare the inter-atomic C-C spacings of the two types of carbonaceous

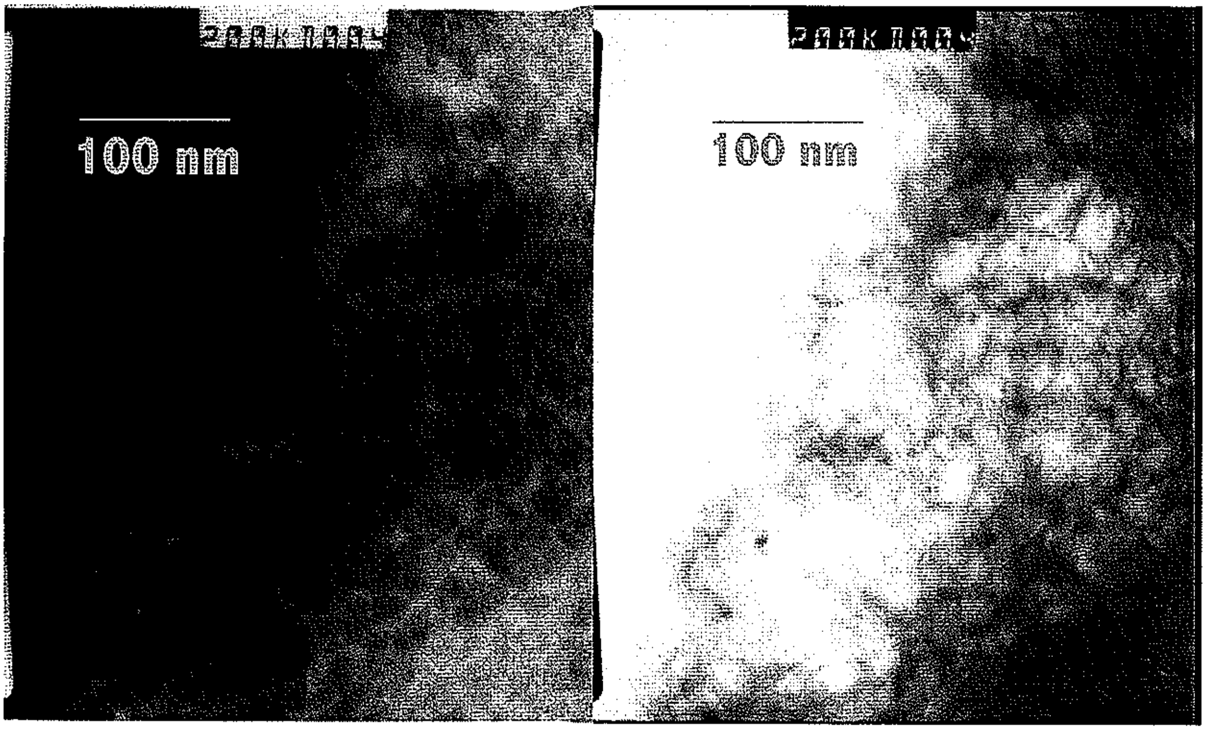

Figure 3. *Higher resolution TEM negatives (left) and brightfield images (right) of a PGC particle taken 20,000x magnification.*

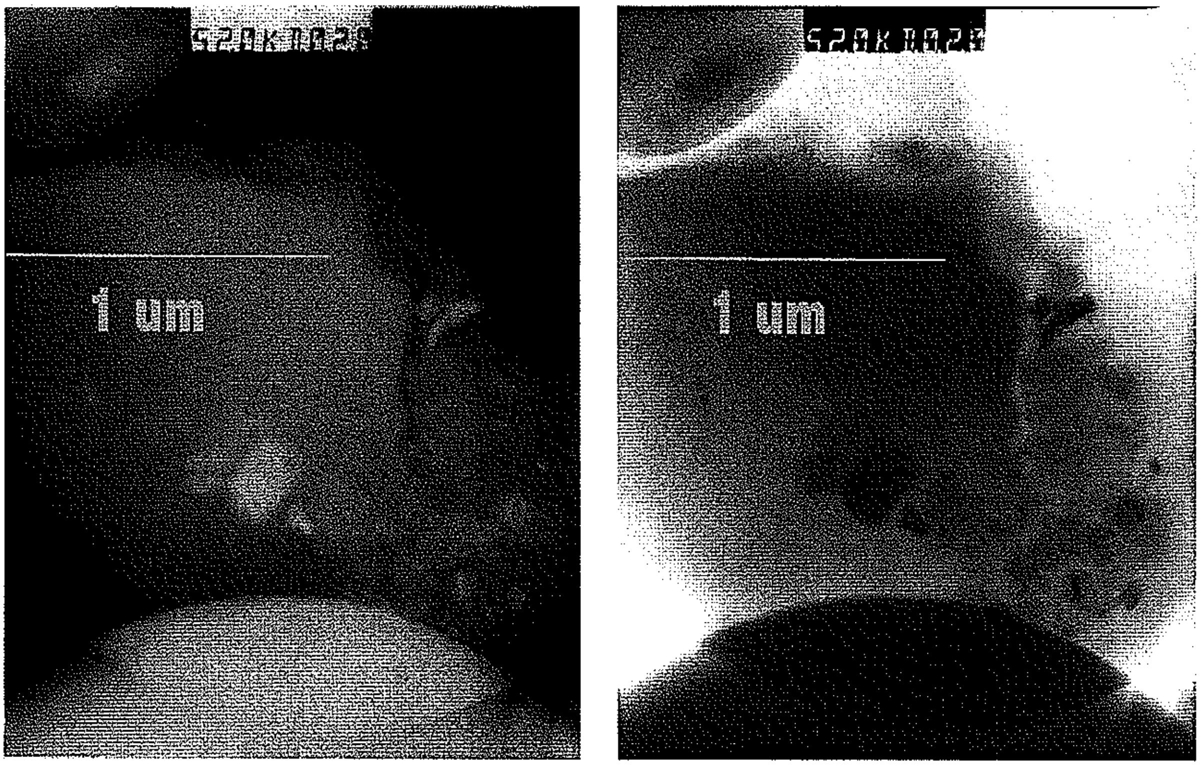

Figure 4. *A higher magnification (56,000x) negative (left) and brightfield image (right) of a GC particle that has been crushed in half*

particles. A good survey of SAED can be found in the TEM textbook by Williams and Carter.[62] Prior to sample analysis, the cameral length for the microscope was calibrated with a polycrystalline material of known inter-atomic distances (polycrystalline gold sputtered onto a copper grid, SPI supplies, West Chester, PA). Under the conditions employed, this calibration yielded a camera constant (λL) of 1.72935 cm-Å. As with the images, the diffraction patterns were digitized with a transmission scanner at a resolution of 600 dpi.

The SAED patterns for both PGC and GC are provided in Figure 5. The ring shapes observed for both PGC and GC arise from the diffraction of electrons from the randomly oriented nanocrystalline/amorphous particles. It is the thickness of these rings that can be used to estimate whether the material is crystalline or amorphous, and it is the diameter across these rings that can be used to determine lattice spacings within the particles. With this in mind, the SAED pattern for PGC consists of finer, more defined rings than those observed for GC. This observation supports the notion that the 'ribbons' observed in Figure 3 for PGC are strands of nanocrystalline graphite, which is consistent with the results found by Knox.[59] In contrast, the broader, more diffuse rings in the SAED pattern for GC hint at a more but not completely amorphous structure. Just the presence of these rings in GC suggests at least some short range order is present, which is consistent with the ribbon structure proposed for glassy carbon and x-ray diffraction studies that observe the stacking of 2-D layers.[63-65]

The experimental values for the lattice spacing were calculated from the camera length equation: $Rd = \lambda L$ (λ is the electron wavelength, L is the camera length, R is radius of the ring, and d is the lattice spacing). The diameter across the rings (pixels) was measured using Image-Pro Express™ software as shown in Figure 5, and converted to the ring radius (cm) in Table 1 based on the resolution in which the patterns were scanned (600 pixels per inch). The calculated lattice spacings obtained from this SAED analysis of PGC and GC are summarized in Table 1, as well as the lattice spacings for indices of graphite that correspond to the closest matching plane.[66]

The lattice spacings calculated from the SAED patterns correlate nicely with that of graphite for both particles. The structure and known inter-atomic spacings for graphite are provided in Figure 6 to assist in interpreting the SAED patterns. The *d*-spacing for the (002) plane for PGC is slightly larger than that for graphite, which corresponds with the spacing

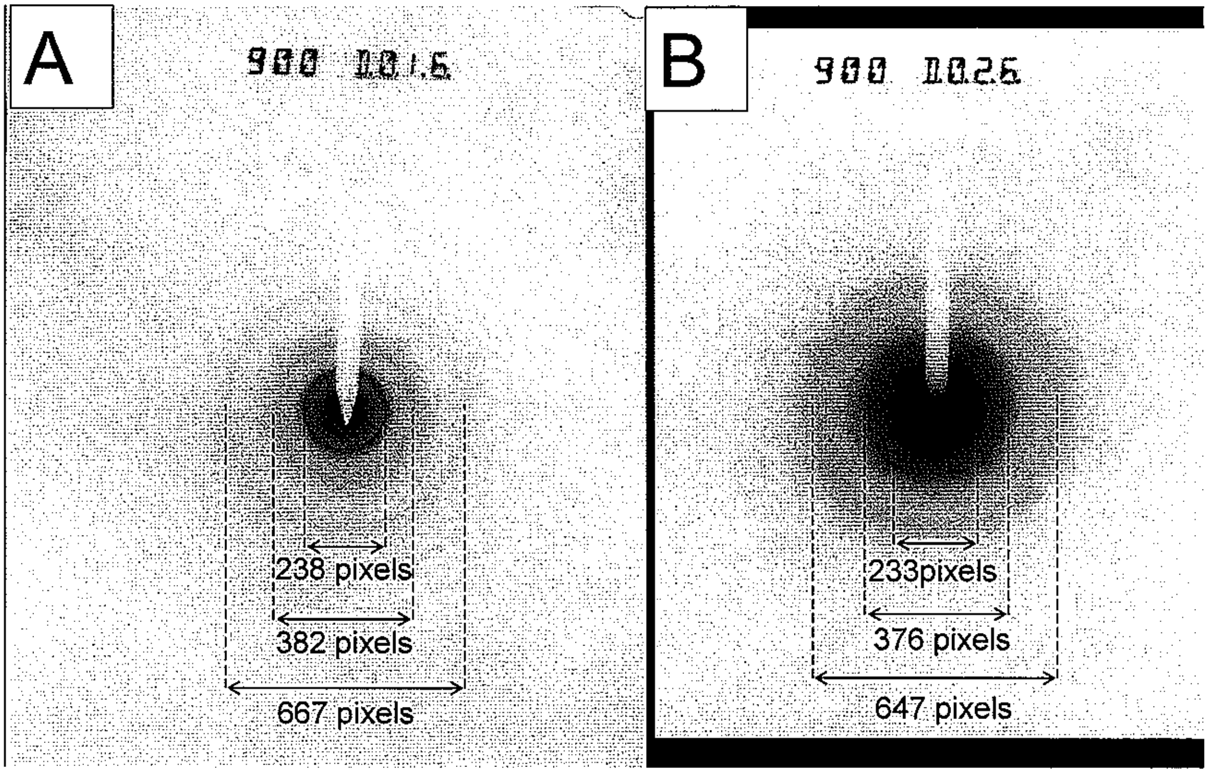

Figure 5. *SAED patterns for a) PGC and b) GC, where the diameters are measured based on the resolution of the scanned images as discussed in the text.*

between adjacent layers *A* and *B* as depicted in Figure 6, and is consistent with the x-ray diffraction lattice spacings reported by Knox.[59] The larger *d*-spacing observed for the (002) plane in GC, is consistent with work by others that show this spacing to be dependent on the time and the temperature involved in production, where the 3.35 Å spacing for graphite is typically not observed until the material has been heated above 3000 °C.[64, 65, 67]

The *d*-spacing for the 110 index, that is the plane that bisects the 60° angle of the unit cell, most closely matches the outermost ring observed in the SAED pattern for both GC and PGC. Furthermore, the d-spacing for the (110) indices predicts the distance between 'meta-' positioned carbon atoms for PGC to be 2.46 Å, and a C-C bond length of 1.42 Å (assume

Table 1. *Comparison of SAED patterns with theoretical spacings of graphite.*

Specimen	Ring Radius (cm)	SAED d-spacing (Å)	Known d-spacing (*hkl*)	(Å)
PGC	1.41	1.23	(110)	1.23
PGC	0.808	2.14	(100)	2.13
PGC	0.505	3.43	(002)	3.35
GC	1.37	1.26	(110)	1.23
GC	0.796	2.17	(100)	2.13
GC	0.496	3.50	(002)	3.35

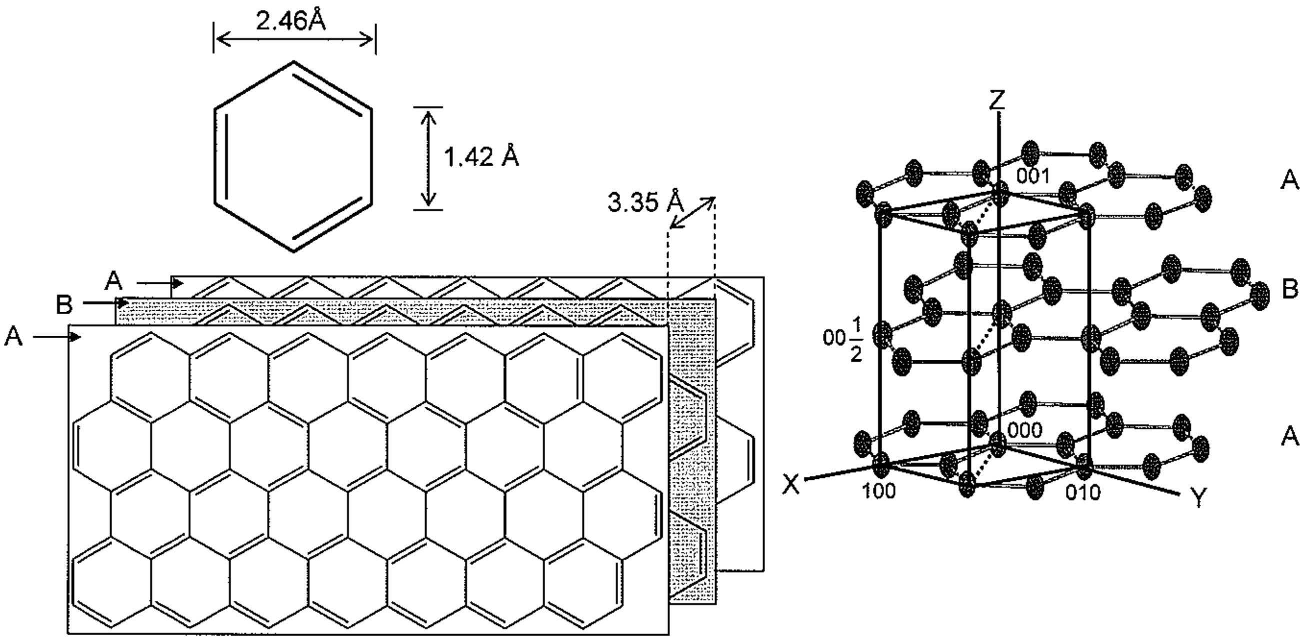

Figure 6. *Graphite dimensions, structure, and unit cell.*

120° angles in the unit cell), which correlate with the theoretical values provided in Figure 6. The (110) spacing for GC, however, points toward bond spacings of 2.53 Å and 1.46 Å for the "meta-" positioned and adjacent carbons, respectively. The longer inter-atomic distances observed for glassy carbon particles are thought to be due to a strained, 2-dimensional structure where the basal plane has shifted relative to the next layer. The *d*-spacing of the intermediate diameter ring for both PGC and GC correlate with the (100) lattice in graphite. Again, the (100) spacing of PGC is closer than that of GC to the theoretical value for graphite, supporting a more graphite-like structure for PGC as opposed to a more amorphous character for GC.

Figure 7 shows a high magnification negative of a GC particle, where one of the previously mentioned higher contrast regions can be observed near the tip of the particle. Convergent beam electron diffraction (CBED) was performed on this region of contrast, and shows this region to possess a highly order structure as hinted at by the diffraction pattern in Figure 7. This diffraction pattern appears as an ordered array of spots that surrounds a dark region near the center in which the electron beam was focused. The theoretical diffraction pattern for crystalline graphite is shown in Figure 8 and was generated using CaRIne© crystallography software (Senlis, France). This theoretical pattern assumes electrons were incident on the sample in the Z-direction of the graphite unit cell. The spacings and angles between spots in the theoretical diffraction pattern coincide with those observed in the CBED pattern in Figure 7, and result from diffraction of electrons by the (100) and (010) planes in the unit cell. Combining this information with the SAED results indicates that GC particles have localized regions of ordered graphite nestled within the larger glassy carbon network.

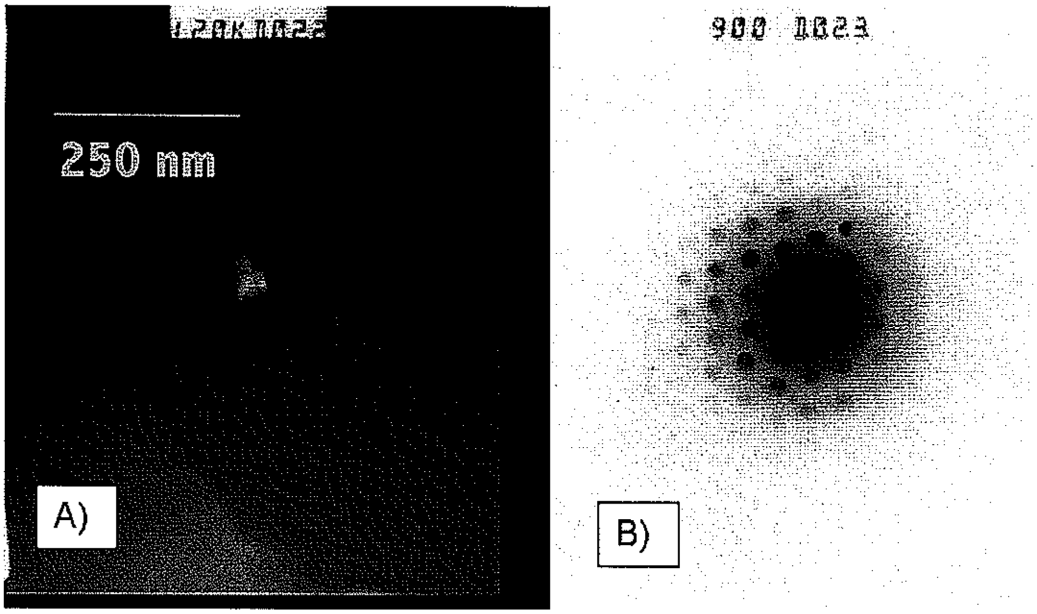

Figure 7. *A) 120,000x image of a large crystallite found in a GC particle. B) CBED pattern obtained from the crystallite shown in A.*

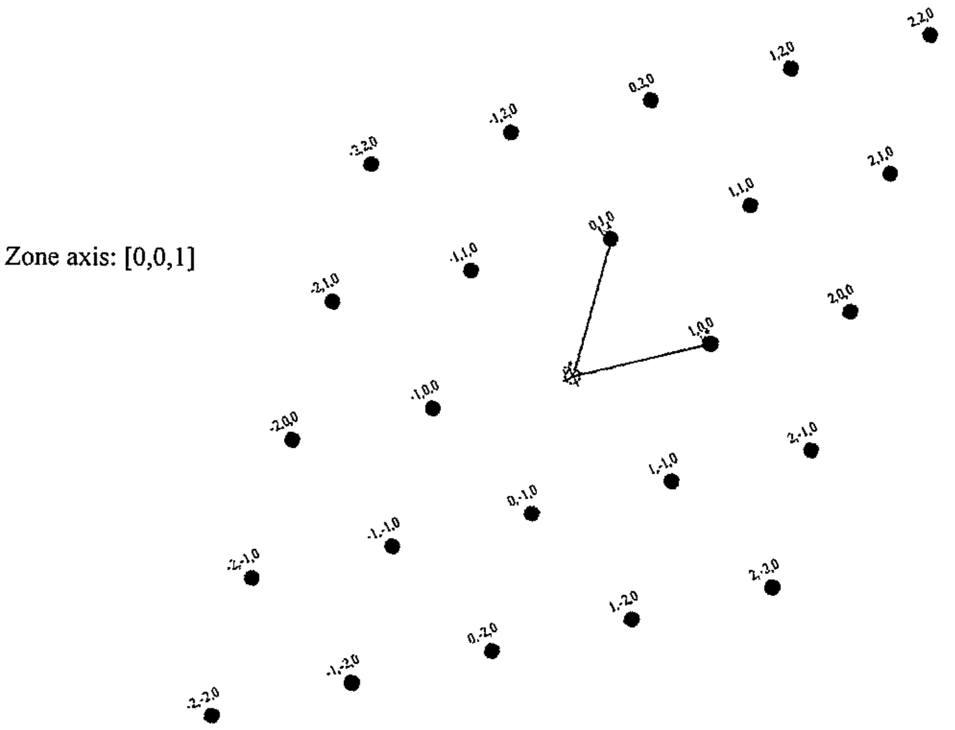

Figure 8. *Computer generated diffraction pattern with the 001 zone axis.*

X-ray diffraction analysis of these carbonaceous materials has been performed, and correlate nicely with the above results.[59, 63, 64] Analysis with x-ray diffraction, however, provides the ability to estimate the dimensions of graphite crystallites through measurements of the angular peak-width for the reflected x-rays, where the width of the (002) diffraction peak estimates the stack height of he graphitic planes, L_c, and the width of the (100) diffraction peak provides an estimate for the basal plane dimensions, L_a. These crystallite dimensions can roughly be estimated by the Sherrer equation:

$$L = k\lambda / B \cos \theta$$

where L is the crystallite dimension, λ is the wavelength of the X-rays, B is the peak width, θ is the Bragg angle of reflection, and k is a constant. In performing this analysis, Knox found PGC to have an L_a of 10 nm and an L_c of 5 nm.[59] In a similar fashion the crystallite sizes for glassy carbon has been shown to be ~3 nm for L_a and ~1 nm for L_c.[68-70]

Raman spectroscopy has also been used to examine the structure and estimate the degree of crystallization for carbon particles.[58, 71-76] Graphite belongs to the $P6_3/mmc$ (D^4_{6h}) space group, where six vibrational modes are possible, of which only two E_{2g} in-plane optical vibrations are predicted by selection rules to be Raman active.[74] The Raman spectra of GC and PGC are shown in Figure 9 using an excitation wavelength of 632.8 nm. The two peaks observed in Figure 9 consist of an E_{2g} peak located at ~1580 cm^{-1} and a graphite disorder induced or "D" peak centered around 1330 cm^{-1}. It should also be noted that the position of the "D" peak is dependent on excitation wavelength,[77] with a shift to lower frequency as excitation wavelength increases. This dependence on excitation wavelength provided evidence that a double resonance scattering process is the source of the disorder peak, where the anisotropy between energy levels of adjacent carbon atoms arises as a consequence of the defect.[75]

The ratio of D:E_{2g} intensities for graphite is thought to be indicative of the dimensions for L_a, and calibration of this ratio to x-ray diffraction data for graphite of variable crystallite sizes has been reported in the literature.[74] In Figure 9, the E_{2g} peak for PGC is larger than the disorder induced peak and gives a D:E_{2g} ratio of 0.63, while the spectrum for GC shows the 1330 cm^{-1} to be the larger with a ratio of 2.37. Comparing these ratios to the calibration curve for graphite,[74] the Raman intensities provide a value of 7.1 nm for the L_a of PGC and 2.2 nm for that of GC, values that compare nicely to the diffraction and imaging data above. While Raman studies for glassy carbon have been performed and correspond with Figure 9,[58] the spectra for PGC compares best to that for nanocrystalline graphite.[73] Not only are the

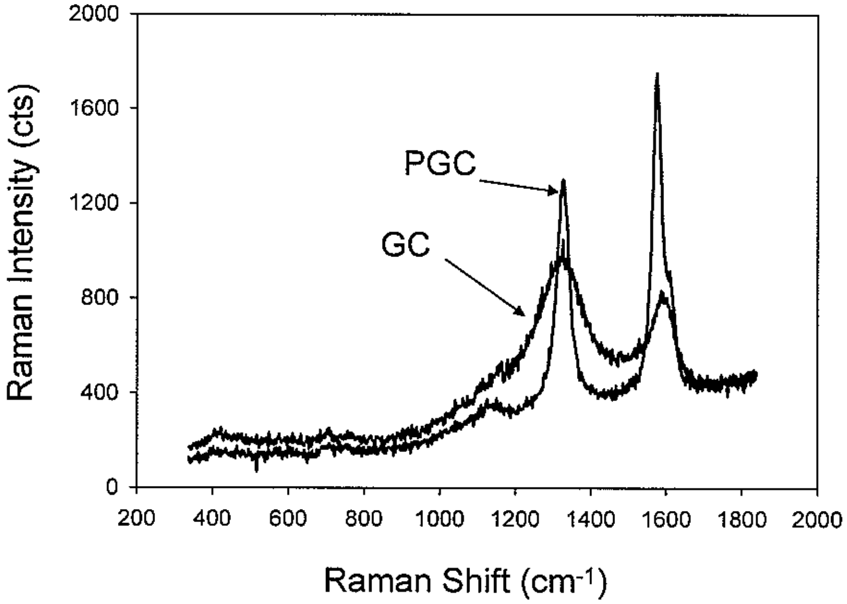

Figure 9. *Raman spectra for GC and PGC particles.*

relative peak heights similar, but the small shoulder on the high frequency side of the E_{2g} peak is present in both PGC and the nanocrystalline graphite powder providing nearly identical spectra.

At this point, the discussion will turn from structural differences between PGC and GC, where a more crystalline nature for PGC was observed compared to GC, to compositional differences found within these particles. The above structural evidence shows the bulk of these particles to be carbonaceous, but it provides little information about the elemental composition at the surface. The chemical composition of the carbonaceous surfaces can be delineated with X-ray photoelectron spectroscopy (XPS) by monitoring binding energies and chemical shifts.[72, 78-80] Figure 10 shows low resolution XPS spectrum for both as received GC (top) and PGC (bottom). From these spectra, a large C1s peak centered at a binding energy of 284 eV and a smaller O1s peak centered at 533 eV are observed for both materials. Quantitatively, normalized peak areas (94.45% C1s and 5.46% O1s) indicate that the GC surface has a greater oxygen content than PGC (99.04% C1s and 0.94 % O1s). This difference is consistent with our structural data in that the more amorphous GC particles are expected to have higher percentage of exposed edge plane carbon. Furthermore, studies of both edge and basal plane of highly ordered pyrolytic graphite (HOPG) have shown that the surface oxygen groups at such a material are present primarily at the edge plane.[55, 81, 82]

Unlike the majority of the carbon atoms on the basal plane, the valency of edge plane carbon atoms are not satisfied by carbon neighbors, and is therefore subject to chemisorption of other elements like hydrogen and the oxygen detected by XPS. These surface oxides have been extensively studied and numerous reviews on this subject have been written.[54, 55, 57, 83, 84]

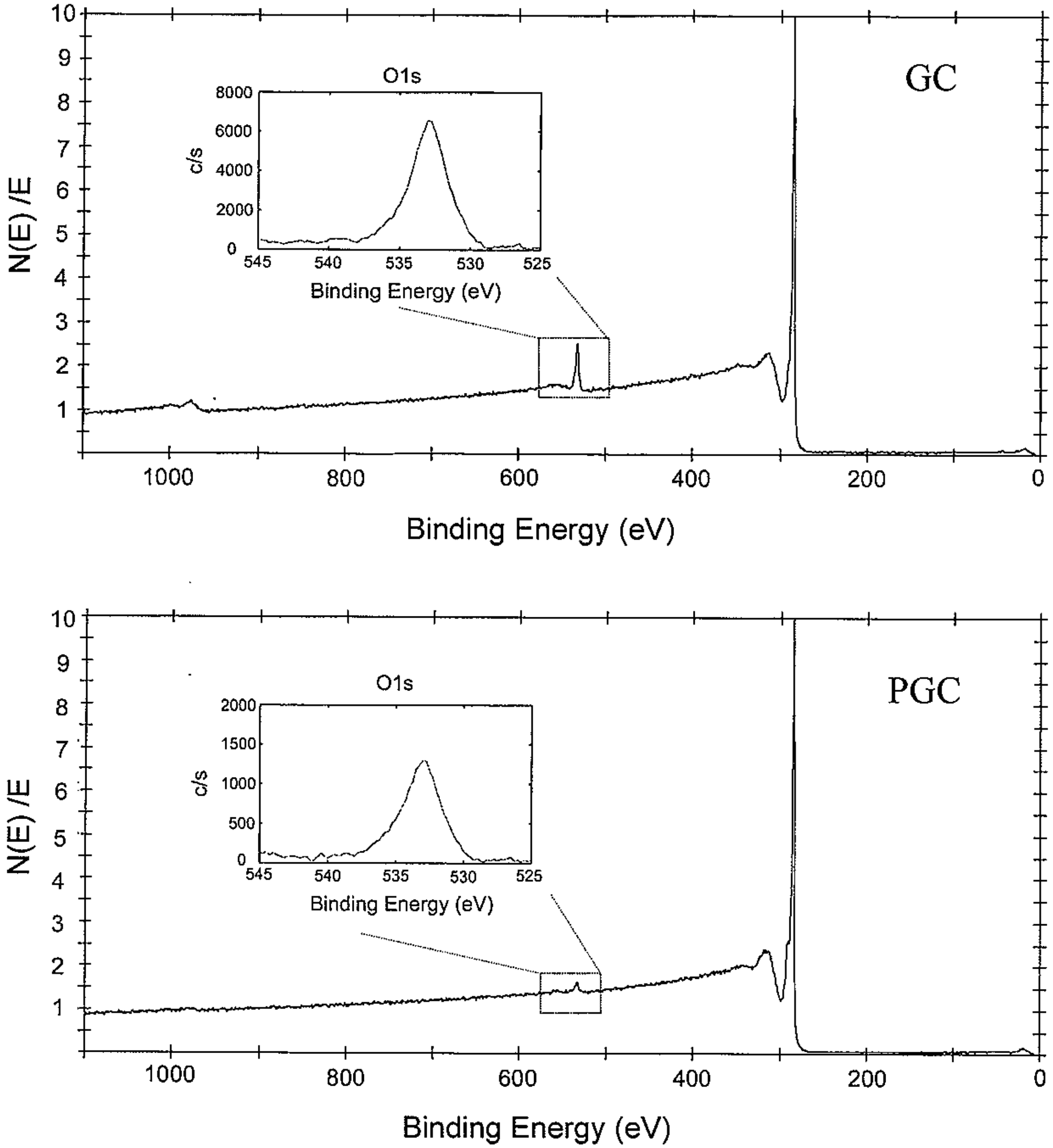

Figure 10. *XPS spectra of carbonaceous stationary phases.*

The structure of these graphite-oxides have been studied by numerous methods, including high resolution XPS, thermal desorption spectroscopy, infrared spectroscopy, solid state ^{13}C NMR, potentiometry, polarography, and acid-base titrations. Results have shown that oxygen is found in a variety of functional groups, including carboxyls, hydroxyls, ethers, phenols, lactones, aldehydes, quinines, and hydroquinones on the carbon surface. Together, the presence of surface bound oxygen groups and the structure of the carbon particles significantly influence analyte adsorption and must be considered when examining retention mechanisms for EMLC-based separations.

Retention mechanisms for carbon-based stationary phases and electrical double layer models for EMLC.

The retention mechanism in EMLC depends on the nature of the solute, as well as properties of the stationary and the mobile phases. In treating retention of these complex systems, chromatographers typically generate a model in which the total retention is the sum of a number of interactions.[8, 85-87] The ability to correlate these models with experimental results stems from descriptors of each interaction via Gibbs free energy as demonstrated in the solvation parameter model.[88-91] In EMLC, analyte retention is envisioned as a combination of electrostatic and non-electrostatic interactions between the solute and the stationary phase. The non-electrostatic contribution to retention may be studied in a similar fashion to retention studies in conventional HPLC systems. The ability to alter the potential applied (E_{app}) to the stationary phase is unique for EMLC and is believed to primarily alter the electrostatic component of retention, and must be accounted for in any retention model.

In utilizing this concept, this section begins by covering some key aspects for the interactions and retention mechanisms believed to govern adsorption onto carbonaceous materials in the absence of an applied potential. The discussion then focuses on how E_{app} influences the model for retention in carbonaceous EMLC columns. This section concludes with an overview of the structure predicted by and the history of electrical double layer (EDL) theory, which will be used in the subsequent data chapters to enhance the description of retention in EMLC.

Retention models for adsorption from liquid mobile phases onto carbon-based stationary phases have been extensively reviewed.[27, 49, 59, 92-95] Retention at these phases is due to a combination of interactions between the solute with the stationary phase, the solute and mobile phase, and the mobile and stationary phases. Initially, carbon-based packings were thought to behave as an ideal hydrophobic reverse-phase material.[59, 96, 97] In reverse phase chromatography, a non-polar stationary phase is used in conjunction with a polar mobile phase, where retention increases with the hydrophobicity of the solute which, in turn, enhances dispersive interactions that attract the solute to the stationary phase.[26]

Work using PGC columns found, however, deviations from this behavior, with polar molecules being more strongly retained than non-polar homologs.[98-101] This polar retention effect of graphite (PREG) was then accounted for by adding a term describing the PREG effect to the reverse phase model.[93, 102] Combining these ideologies, the intermolecular forces believed most descriptive for solute retention on carbon based stationary phases include dispersive interactions between solute-mobile phase, dispersive interactions between solute-stationary phase and donor-acceptor/charge-transfer interactions of the analyte with the carbon surface.[103-105]

The dispersive interactions between the solute and the carbon surface are typically viewed as being non-specific. For reversed phase chromatographic systems, the presence of dispersive forces explains the increase in retention observed when the carbon chain of a functional group on the solute is elongated for a homolog series of small aromatic solutes.[8, 94] These and related studies have shown that retention at PGC follows the linear behavior described by equation 1:[96, 106, 107]

[1] $\log_{10} k' = \beta + \alpha n$

where k' is the retention factor, β is the theoretical log k' for benzene, α is a measure of the change in retention for solutes possessing an aliphatic side group with carbon number n. Furthermore, these experiments found that PGC stationary phases are more sensitive to carbon chain length than more traditional reverse phase columns.

Solute-solvent dispersive interactions also play an important role in the retention process. The eluotropic series for a variety of mobile phase solvents on carbon columns have been studied and the results show no discernable trends.[48, 49, 97, 108-111] However, in mixed aqueous-organic solvent systems, retention for small aromatic molecules typically decreases at higher percentages of organic modifier as described by Equation 2:[102, 112-115]

[2] $\log_{10} k' = \log_{10} k_w - bC_{org}$

where k_w is the capacity factor when the mobile phase is composed of pure water, C_{org} is the percentage of organic modifier, and b denotes the sensitivity of solute retention toward C_{org}. The retention parameters in Equation 2 have been monitored for a series of solute molecules and have been shown to correlate with molecular polarity parameters of the solute.[94]

Ever since their use in gas chromatography, carbonaceous stationary phases have been shown to be effective in the resolution of structural isomers.[40, 116] Similar behavior has also been observed in PGC columns, in which this selectivity has been attributed to differences in the ability to interact with the surface based on geometric constraints.[111] That is, the structural isomer that can best align with the flat stationary phase surface exhibits longer retention than rigid, less planar isomers. Furthermore, this notion implies that a significant component of retention arises due to interactions of the solute with the flat basal plane.

It was previously mentioned that retention increases with increasing solute polarity on carbonaceous stationary phases, the PREG effect.[98-101, 117] It has also been shown that carbon stationary phases can be used to separate both inorganic and organic ions.[60, 93, 101, 118-122] The use of donor-acceptor, or charge induced, interactions in which a polar or charged solute induces a "mirror charge" in the delocalized π electrons of the carbon surface has been used to explain this effect. This induced dipole or charge leads to an electrostatic attraction, which contributes to the aforementioned PREG effect. A method to quantitatively measure the PREG effect has been proposed that compares the retention of polar compounds with their aliphatic analogs in which an interaction energy of up to 42 kJ/mol (compare to ~20 kJ/mol for hydrogen bonds) was found.[93] Like the model to describe the stereoselectivity of PGC, the use of delocalized π-electrons to explain this effect implies that these interactions occur primarily on the basal plane.

Another factor that must be considered in retention on carbon phases is the presence of oxygen-containing functional groups on the carbon surfaces. In contrast to the belief that adsorption primarily occurs onto the basal plane, electrochemical analysis using HOPG has shown that the edge plane appears to be the primary adsorption site for polar and charged solutes.[123-126] The influence of oxygen on retention has only recently been noticed through studies that have shown retention to change with the presence of redox agents on a PGC column.[127-131] While the percent of oxygen on the surface is small, changes in the amount or structure of chemisorbed oxygen over time have been used to explain slow equilibration times and drifts in retention.

The currently held belief that retention on carbon stationary phases is a result of the hydrophobic, dispersive, and donor-acceptor forces discussed above is valid when an E_{app} is imparted on the stationary phase, as in EMLC. The retention mechanisms for EMLC have recently been reviewed, and vary greatly from system to system depending on the nature and reactivity of the support material as well as the electrochemical activity and charge of the solutes.[11, 17] The remainder of this section highlights models that detail the influence of E_{app} on retention in EMLC-based separations. The data chapters to follow will then build upon this information using experimental evidence to expand the scope of some of these empirical models.

Applying a potential to the stationary phase is typically viewed to influence solute retention in one of two ways: through a redox transformation mechanism or through electrostatic interactions with the surface.[11] The redox transformation mechanism can be used to describe the influence of E_{app} in systems containing either an electroactive solute, support, or mobile phase component.[5, 18, 28-30, 132, 133] Recent work in EMLC has focused primarily on systems in which changes in E_{app} are believed to alter retention for small aromatic compounds by modifying the strength of electrostatic interactions with the stationary phase.[9, 10, 15, 16, 18-23] In this model, electrostatic attractions and repulsions between the solute and the carbon surface are envisioned to change with E_{app}. As such, when E_{app} is positive of the potential of zero charge (PZC) for the carbon support, retention for anions is expected to increase while that for the cations should decrease. The opposite should hold true for E_{app} negative of the PZC.

The effect of this electrostatic interaction on retention is commonly summarized through plots of the logarithmic relationship between E_{app} and k'. When plots of ln k' versus E_{app} are linear, the retention dependence can be explained in terms of the influence of an electric field on a Boltzmann distribution of ions as a function of distance from electrode surface. However, if a neutral analyte exhibits a potential dependant retention or if the relationship between ln k' and E_{app} for a charged analyte is non-linear, this first level model fails and must be revised.[15-17] The first step in this revision involves describing how this anomalous behavior could arise due to changes imparted by E_{app} on the magnitude of the donor-acceptor interactions observed in non EMLC columns. To this end, values for the Hansch hydrophobicity,[134] Hammet electronic,[134] and Charton steric[135] parameters as well as molecular volume considerations were compared to the slope of ln k' versus E_{app}, similar to the work on non-EMLC columns, where polarity parameters were deemed important.[16, 94]

An adsorption molecular model that accounts for a multitude of solute/solvent types and considers the effect of E_{app} on retention in EMLC has been presented.[136] In some circumstances, this model predicts anomalous changes in ln k' with E_{app} for neutral solutes, and in other instances it does predict the irregular behavior in which cations act as anions (and vice versa). At the same time, a quadratic relationship between ln k' and E_{app} is predicted for neutral and monovalent solutes in a mobile phase containing 1:1 supporting electrolyte, and not the linear relationship commonly observed.

At this point in the development of EMLC retention mechanisms, both the molecular adsorption approach and the electrostatic interaction approach have their merits and disadvantages. In bridging these two models, the structure and behavior of solute, solvent, electrolyte, at electrode-solution interfaces as a function of E_{app} is typically examined with electrical double layer (EDL) theory. The goal of EDL theory is to model the structure and distribution of charge at interfaces. In the context of EMLC, these charges could be solute or electrolyte molecules in the mobile phase or electrons within the stationary phase.

In general, the double layer is viewed as an arrangement of charged species and oriented dipoles at electrode-solution interfaces.[137] Numerous electrochemistry, adsorption and colloid science textbooks have reviewed this topic, and the survey below provides a brief overview of the major developments in this theory,[138-142] and then discusses the influence of double layer theory in separation sciences. The simplest model for electrical double layers is the Helmholtz,[143] or parallel plate condenser model. This model describes the formation of a single layer of ions in solution that counters the charge on the stationary phase. The next advancement in double layer models, the Gouy-Chapman (G-C) theory accounted for the thermal distribution of ions in the double layer.[144, 145] G-C theory combines a Boltzmann distribution function with the Poisson equation, which describes the location of charge as a function of distance from the electrode surface. Taken together, the Poisson-Boltzmann equation describes an exponential drop in charge as a function of distance from the electrode surface. This theory was soon modified by Stern to remove the point charge approximation.[146] The Stern modification separated the charge in solution into both a parallel plate and a diffuse component, such that these two regions can be treated as capacitors in series.

Since these early works, electrical double layer theory has expanded to account for solvent adsorption, solvent orientation, specific as well as non-specific adsorption of both ions and neutrals, as well as electronic properties and composition of the electrode.[137, 138] The modern picture of the solution side of electrode-solution interfaces consists of several layers: the inner Helmholtz plane (IHP), the outer Helmholtz plane (OHP), and the diffuse layer. A linear potential drop is observed across the IHP which contains highly ordered solvent molecules and specifically adsorbed solutes. The potential also decreases in a linear manner when moving away from the electrode across the OHP that is composed of solvated ions and solvent molecules. The diffuse layer, in contrast, is a region between the OHP and bulk solution that contains any remaining charge in order to ensure electroneutrality of the interface, and is described by an exponential decrease in potential with distance from the electrode.

Most, if not all, analytical separation systems require the presence of some sort of interface and would therefore be influenced by the double layer in some way. For EMLC, the work herein uses double layer theory to describe the charging and adsorption of ions onto the stationary phase surface as a function of E_{app}. Similarily, in ion-exchange and ion-pair chromatography, EDL theory has been used to describe ion retention but as a function of the stationary phase's surface charge rather than the applied potential.[147-153] EDL theory has also been used to describe many electrokinetic phenomena that are the basis of a variety of electromigration separation techniques. A good basis for the uses of EDL theory to describe these phenomena can be found in many colloid science, electrophoresis and electrochemistry texts.[8, 138, 142, 154, 155] EDL theory is also essential to separations of colloidal suspensions in which DVLO (Deryagin-Landau-Verwey-Overbeek)[156, 157] theory uses EDL theory to describe the charge surrounding the colloidal solutes as a means to understand their electrophoretic mobility. In many instances the presence of double layers are beneficial to the separation system and other times the presence of these double layers can be counter-productive (e.g. electrochemical conductivity detectors where sensitivity may be compromised through charging effects).

Through this review, the basic premise of EMLC, the structure and composition of the carbon-based stationary phases employed, the retention mechanisms believed to govern retention on carbon based stationary phases, as well as the basics ideas in EDL theory have been presented. In the following chapters, EMLC will be investigated such that many correlations between the concepts and theories presented herein and the performance of EMLC columns will be drawn. In so doing, EMLC will prove itself beneficial both to the separation sciences and to interfacial electrochemistry.

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CHAPTER 2. ELECTRICAL DOUBLE LAYER THEORY IN ELECTROCHEMICALLY MODULATED LIQUID CHROMATOGRAPHY

A paper to be submitted to *The Journal of Chromatography A*

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ABSTRACT

The role of the supporting electrolyte in separations using electrochemically modulated liquid chromatography (EMLC) has been investigated. An analysis of the change in analyte retention with the identity and concentration of supporting electrolyte has been performed and the results were used to extend the understanding of EMLC-based retention. Analysis of this contrast in behavior in the context of Gouy-Chapman diffuse double layer theory reveals insights into a retention mechanism that depends on the potential applied to the stationary phase and on the charge of the solute injected. At potentials positive of the PZC, an ion-exchange mechanism is postulated for the retention of negatively charged solutes. At potentials close to the PZC, the electrostatic model no longer describes analyte retention. Instead, the predominant retention mechanism likely involves the hydrophobic interactions with the carbonaceous stationary phases. These findings are demonstrated by using a temporal gradient in supporting electrolyte concentration to optimize an EMLC separation.

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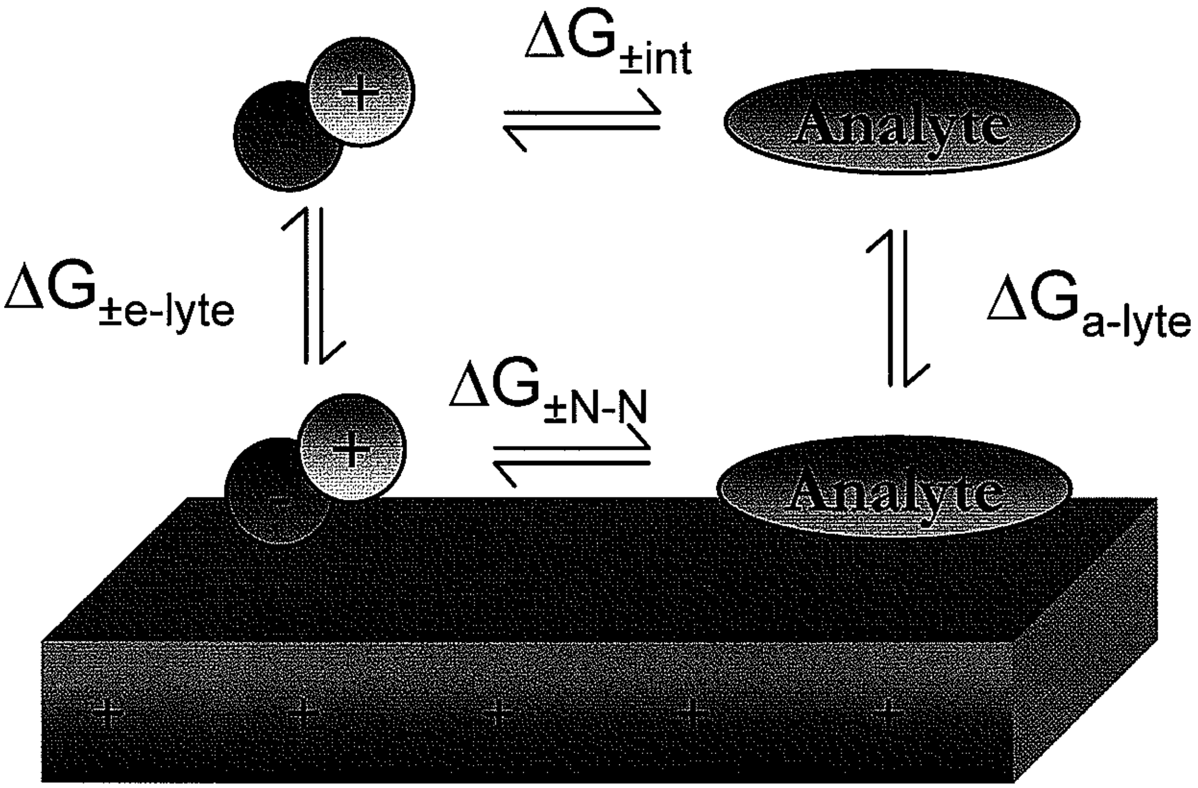
INTRODUCTION

Electrochemically Modulated Liquid Chromatography (EMLC) is a unique union of electrochemistry and chromatography.[1, 2] This union is accomplished by using a conductive stationary phase (e.g., glassy carbon (GC) or porous graphitic carbon (PGC)) as the working electrode in a three-electrode electrochemical cell that is also configured as the stationary phase of a LC column. Changes in the potential applied (E_{app}) to the stationary phase can therefore be employed to manipulate the efficiency of a separation in a manner likened to that of mobile phase gradients in liquid chromatography. EMLC has been applied to the separation of a wide range of mixtures, including aromatic sulfonates,[3-5] monosubstituted benzenes,[6] dansylated amino acids,[7] corticosteroids,[8, 9] benzodiazepines,[9, 10] the enantiomers of hexabarbital and mephenytoin,[11] short chain alkanoic acids,[12] and metal ion complexes.[13]

EMLC differs from conventional LC because the effective composition of the stationary phase can be controlled. However, to do so effectively requires the presence of a supporting electrolyte in the mobile phase. In electrochemistry, the supporting electrolyte performs three important functions: 1) it increases solution conductivity; 2) it minimizes migration effects; and 3) it creates a reproducible electrical double layer.[14] In addition to serving the same purposes in EMLC, the supporting electrolyte can have an impact on separation efficiency through the types and magnitude of interactions with the analyte. For example, components of the supporting electrolyte may compete with the analyte for adsorption sites on the stationary phase. This paper is therefore the first in a series of investigations that are aimed at delineating the role of supporting electrolyte in EMLC separations, and ultimately, the retention mechanism in EMLC.

In EMLC, the influence of E_{app} on retention is commonly summarized by monitoring changes in the capacity factor (k'). A plot of the log of k' versus E_{app} (i.e., a capacity-potential curve) is linear when the retention is dominated by electrostatic interactions, behaving as a Boltzmann distribution of ions in an electric field.[7, 15] This behavior is common for small ions including many aromatic sulfonates. Other analytes, however, exhibit a nonlinear capacity-potential curve, including uncharged molecules and to a lesser extent, some charged analytes. These examples serve as evidence that the pure electrostatics model must be refined.[16] To this end, the work detailed herein extends the electrostatic model using Gouy-Chapman diffuse double layer theory to account for competition for adsorption sites between the supporting electrolyte and analyte as a function of E_{app}.

Scheme 1 illustrates several of the pathways in which supporting electrolyte may influence retention from a thermodynamic standpoint. The competition between supporting electrolyte and analyte for adsorption sites on the stationary phase is shown. Moreover, interactions between an electrolyte ion and the analyte on the stationary phase and in the mobile phase are represented. Thus, the overall free energy of adsorption for an analyte (ΔG_{tot}) is a combination of the free energies of interactions between all species in the system and is manifested in the chromatographic retention of the analyte. The interactions that occur directly between the analyte and the surface of the stationary phase are defined as $\Delta G_{a\text{-}lyte}$ and include, for example, the hydrophobic and donor-acceptor interactions. The free energy for adsorption of supporting electrolyte is defined by $\Delta G_{\pm e\text{-}lyte}$. This term can be split into electrolyte cations, $\Delta G_{+e\text{-}lyte}$, and electrolyte anions, $\Delta G_{-e\text{-}lyte}$. The free energy of interaction between an analyte and surface-bound supporting electrolyte is given by $\Delta G_{+N\text{-}N}$ for cations



$$\Delta G_{tot} = \Delta G_{a\text{-}lyte} + \Delta G_{\pm N\text{-}N} - \Delta G_{\pm e\text{-}lyte} - \Delta G_{\pm int} + \Delta G_{sol}$$

Scheme 1. *Thermodynamic interactions describing the influence of supporting electrolyte on adsorption onto the stationary phase in an EMLC experiment (see text for details).*

and ΔG_{-N-N} for anions, note that these interactions are differ from those of the same species occurring in bulk solution (ΔG_{+int} for cations or ΔG_{-int} for anions). For simplicity, Scheme 1 neglects the presence of oxygen containing functional groups on the carbon surface and omits the role of mobile phase solvent, ΔG_{sol}. The effect of oxygen containing functional groups on retention on PGC stationary phases warrants further study.[13, 17-19] On the other hand, the general role of solvent and organic modifiers on retention has been studied extensively for PGC stationary phases in conventional HPLC experiments.[20-25] Temperature studies in EMLC have recently shown that changes in retention as a function of E_{app} are entropically driven and further demonstrate the need for progress in the retention model.[26] Taken together, these factors show that the possible contributions to retention in EMLC are complex, and demonstrate the need to determine the contributions which dominate system behavior.

In this paper, insights into the retention mechanism are advanced with respect to an assessment of the role of supporting electrolytes. We have therefore monitored changes in retention as the supporting electrolyte concentration and composition are systematically varied. To facilitate this analysis, the Gouy-Chapman (G-C) double layer theory is adapted for use with the chromatographic data provided by EMLC. This electrostatic retention model is compared to models developed for ion-pair chromatography using similar adaptations of electrical double layer theory.

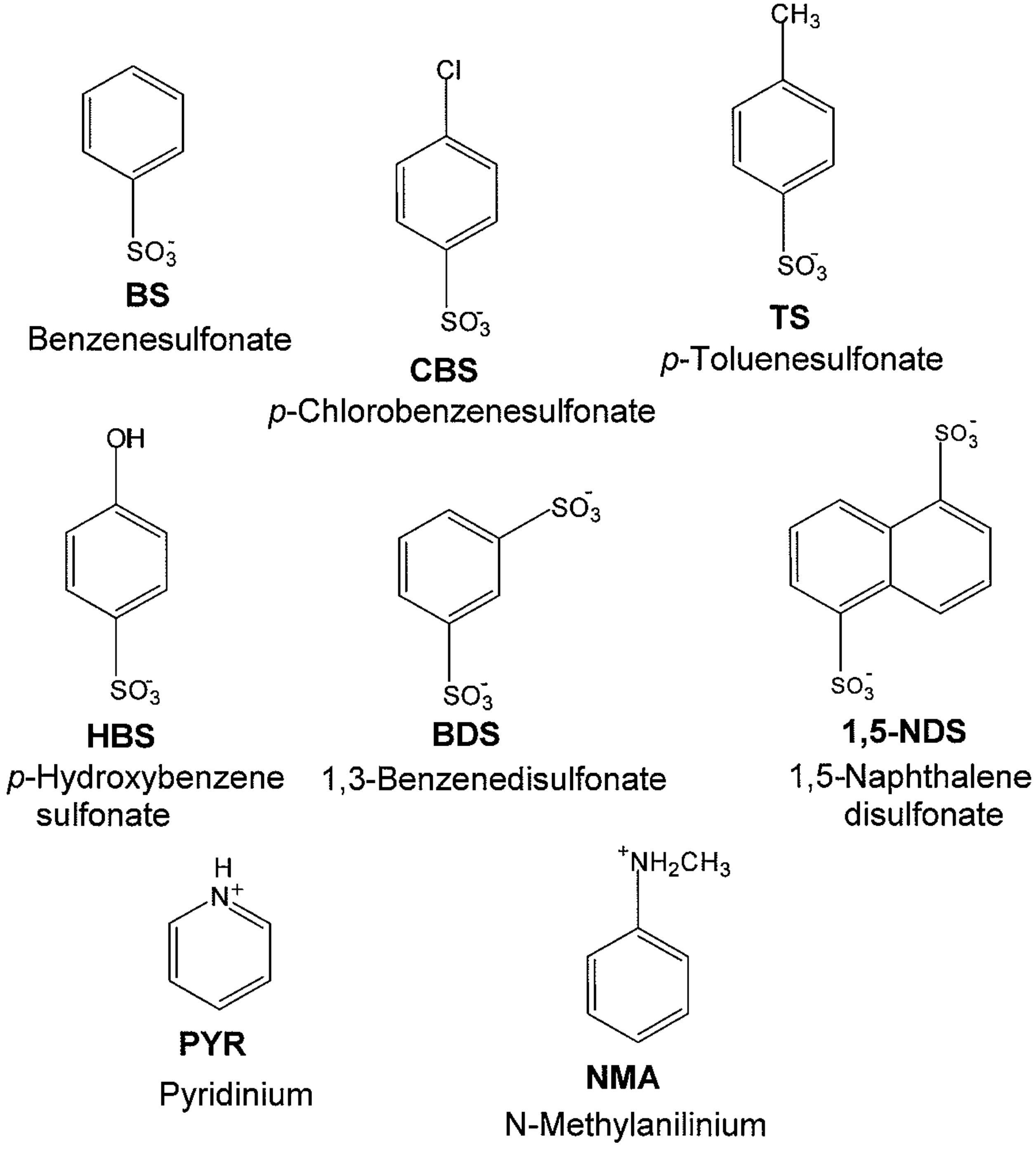
EXPERIMENTAL SECTION

Chemicals

The structures of the test analytes and their acronyms are shown in Figure 1. Importantly, in probing the influence of supporting electrolyte on retention in EMLC, it is imperative that the analyte is electroinactive over the experimental range of E_{app}. With the exception of hydroxy benzene sulfonate (HBS) case below, all other test analytes in Figure 1 were shown to meet this criterion in previous reports.[7, 15] Sodium benzenesulfonate (BS), sodium *p*-toluenesulfonate (TS), pyridine (PYR), disodium 1,3-benzenedisulfonate (BDS), sodium *p*-hydroxybenzenesulfonate (HBS), trifluoroacetic acid (TFA), dibromomethane, and lithium perchlorate were purchased from Aldrich (Milwaukee, WI, USA). Sodium *p*-chlorobenzenesulfonate (CBS) was obtained from TCI America (Portland, OR, USA). N-methylaniline (NMA) and disodium 1,5-naphthalenedisulfonate (1,5-NDS) were acquired from Eastman Kodak (Rochester, NY, USA). Acetonitrile and sodium fluoride were purchased from Fisher Scientific (Fair Lawn, NJ, USA). All chemicals were used as received. Distilled water was further purified with a Millipore Milli-Q system (Bedford, MA, USA). Before use, the solutions were filtered through a 0.5-μm filter (GE Osmonics, Minnetonka, MN, USA), and thoroughly degassed by sparging with helium.

EMLC Columns

The design and construction of the column have been described in detail elsewhere.[3] In short, these columns consist of a Nafion cation-exchange membrane in tubular form (Perma Pure Inc., Toms River, NJ, USA) that is inserted inside a porous stainless steel cylinder (Mott Metallurgical Inc., Farmington, CT, USA). The column is slurry packed



BS
Benzenesulfonate

CBS
p-Chlorobenzenesulfonate

TS
p-Toluenesulfonate

HBS
p-Hydroxybenzene sulfonate

BDS
1,3-Benzenedisulfonate

1,5-NDS
1,5-Naphthalene disulfonate

PYR
Pyridinium

NMA
N-Methylanilinium

Figure 1. *Analyte structures and their acronyms.*

with porous graphitic carbon (PGC; ThermoHypersil, Bellefonte, PA, USA), which functions as both a working electrode and stationary phase. The porous stainless steel cylinder prevents deformation of the Nafion tubing under the high pressure of chromatographic flow and is also used as the auxiliary electrode. The Nafion tubing serves three important functions: it acts as a container for the stationary and mobile phases, as an electron insulator to prevent short-circuits between the auxiliary and the working electrode, and as a salt bridge between the internal mobile phase and an external electrolyte reservoir. The external electrolyte reservoir houses a Ag/AgCl saturated NaCl reference electrode.

The experiments employed 5-μm diameter PGC particles as the stationary phase. The PGC has been characterized by X-ray photoelectron spectroscopy and found to be devoid of any detectable oxygen-containing functional groups (estimated detection limit: 0.2 atomic %).[5] The manufacturer has estimated the nominal pore diameter to be ~250 Å, which yields a porosity of ~80% for the PGC particles.[27] The surface area of the porous graphitic carbon stationary phase is *ca.* 30 m^2 based on BET adsorption measurements (120 m^2/gram)[28] and the amount of PGC packed into the column (~0.25 g).

Instrumentation

Chromatographic experiments were performed using a HP 1050 series module HPLC equipped with a solvent cabinet, a quaternary pumping system and a diode array detector (Hewlett-Packard, Santa Clara, CA, USA). Sample solutions were injected via a Rheodyne Model 7125 injector with a 5-µL sample loop (Cotati, CA, USA). The potential of the working electrode was controlled using either an AMEL Instruments Model 2055 High-Power Potentiostat (Milan, Italy) or a Model 174A Polarographic Analyzer (Princeton

Applied Research, Princeton, NJ, USA). The pH of the aqueous phases before mixing with acetonitrile was determined using an Orion model 520A pH meter (Beverly, MA, USA).

Mode of Operation

In examining the effect of supporting electrolyte concentration on the separation of aromatic sulfonates, on-line mixing of water, aqueous salt solutions, and acetonitrile was used to carefully manipulate the mobile phase composition. Trifluoroacetic acid (TFA) was added to all the salt solutions and water in proportions to set the pH at ~3 for sample mixtures that contained pyridine (pK_a=5.24) or N-methyl aniline (pK_a=5.23);[29] this pH level ensures that both analytes are present as monovalent cations in the mixed solvent mobile phase. When the composition of the mobile phase was changed, the system was allowed to reach a steady state under the new conditions by the longer of the following two scenarios: the detector baseline became stable or 30 min after the change in conditions. The absorbance of all analytes was monitored at 220 nm unless otherwise noted. Individual injections of each analyte were performed for peak identification in the separation of mixtures, and a water blank was used to determine the solvent front for calculating k'. The retention times for determining k' were determined from the first statistical moment[30-32] of the chromatographic peak in order to compensate for tailing.

RESULTS AND DISCUSSION

Effect of applied potential

The effect of E_{app} on the separation of a three-component mixture of aromatic sulfonates is presented in Figure 2 for values of E_{app} ranging from +200 to –600 mV.[3-5] As is

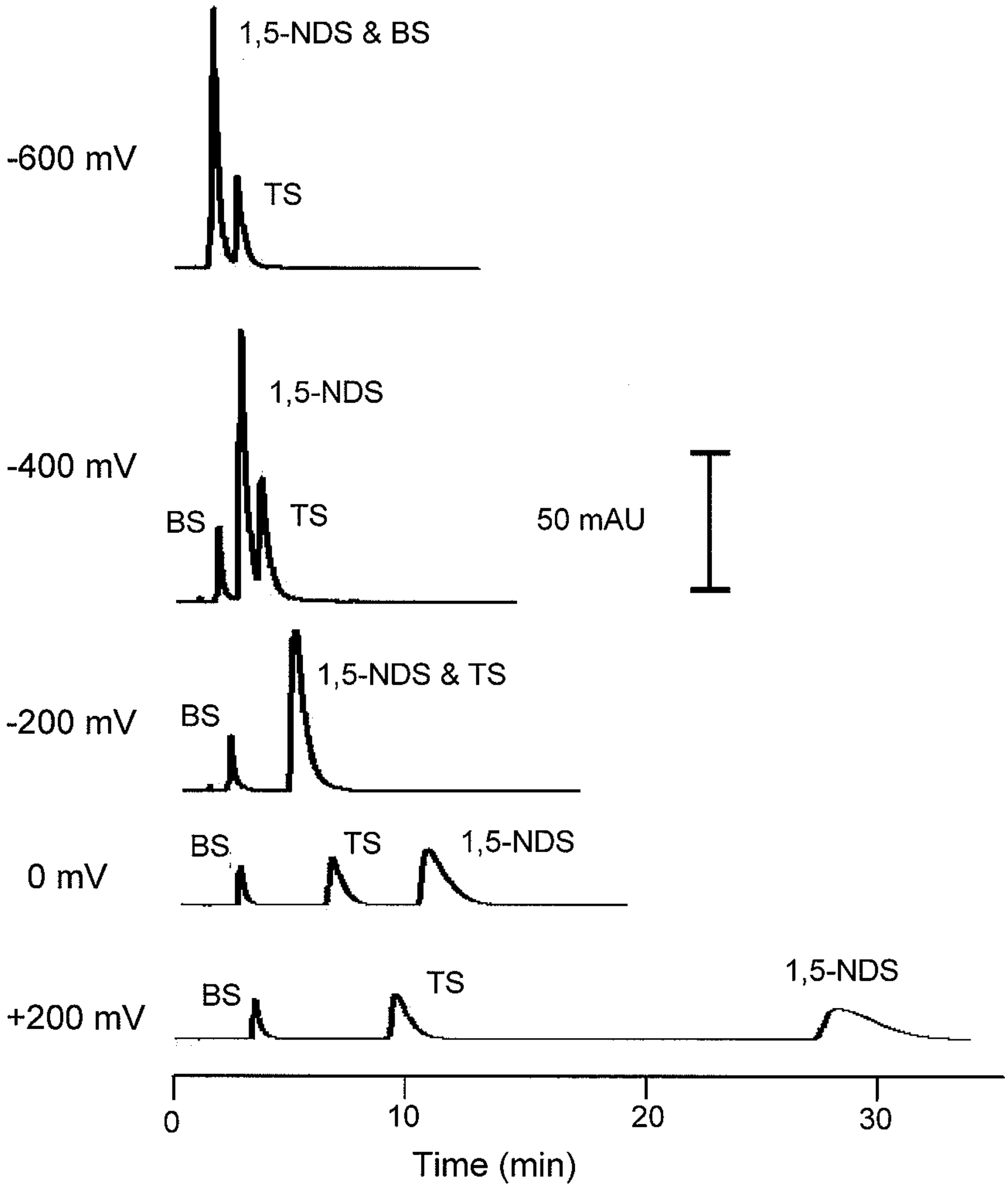


Figure 2 *Chromatograms illustrating the influence of E_{app} (versus Ag/AgCl sat'd NaCl) on the separation of BS (10 μM), TS (18 μM), and 1,5-NDS (30 μM). The mobile phase consists of 0.1 M lithium perchlorate and 10% acetonitrile in water. The flow Rate is 0.4 mL/min.*

evident, all analytes show an increase in retention as E_{app} becomes more positive. The observed trends follow expectations based electrostatic interactions of negatively charged compounds with a charged stationary phase. However, the sensitivity of retention for each analyte to changes in E_{app} varies. BS, for example, undergoes a change in k' from 0.60 at -600 mV to 2.69 at +200 mV, a change in retention time of ~2 min. 1,5-NDS, in contrast, is much more sensitive to changes in E_{app}. With 1,5-NDS, k' changes from 0.76 at –600 mV to 29.93 at +200 mV, a 25 min increase in elution time.

The difference in how E_{app} affects the retention of individual analytes also demonstrates the ability of EMLC to alter the elution order of a group of structurally similar analytes. For instance, the elution order is 1,5-NDS $\cong$ BS < TS at –600 mV, BS < 1,5-NDS < TS at -400 mV, BS < 1,5-NDS $\cong$ TS at -200 mV, and BS < TS < 1,5-NDS at both 0 and +200 mV. As demonstrated previously,[3-5] changes in the elution order as a function of E_{app} present an intriguing variation in the capability for the manipulation of the effectiveness of an EMLC separation.

The modulation of the retention for all eight compounds is summarized in Figure 3 through capacity-potential curves. The error bars for the values of ln k' are roughly the size of the data symbols and characterize the precision for five replicate injections. With the exception of HBS, each compound follows the linear dependence predicted by the influence of an electric field on a Boltzmann distribution of ions.[33] Linearity also indicates that the analytes are electroinactive under these experimental conditions, further supporting the assertion that changes in retention are driven by electrostatic interactions.

The correlation coefficients for the plots in Figure 3 are provided in Table 1, and support the linearity of the ln k' versus E_{app} relationship. In contrast, the break in the plot for

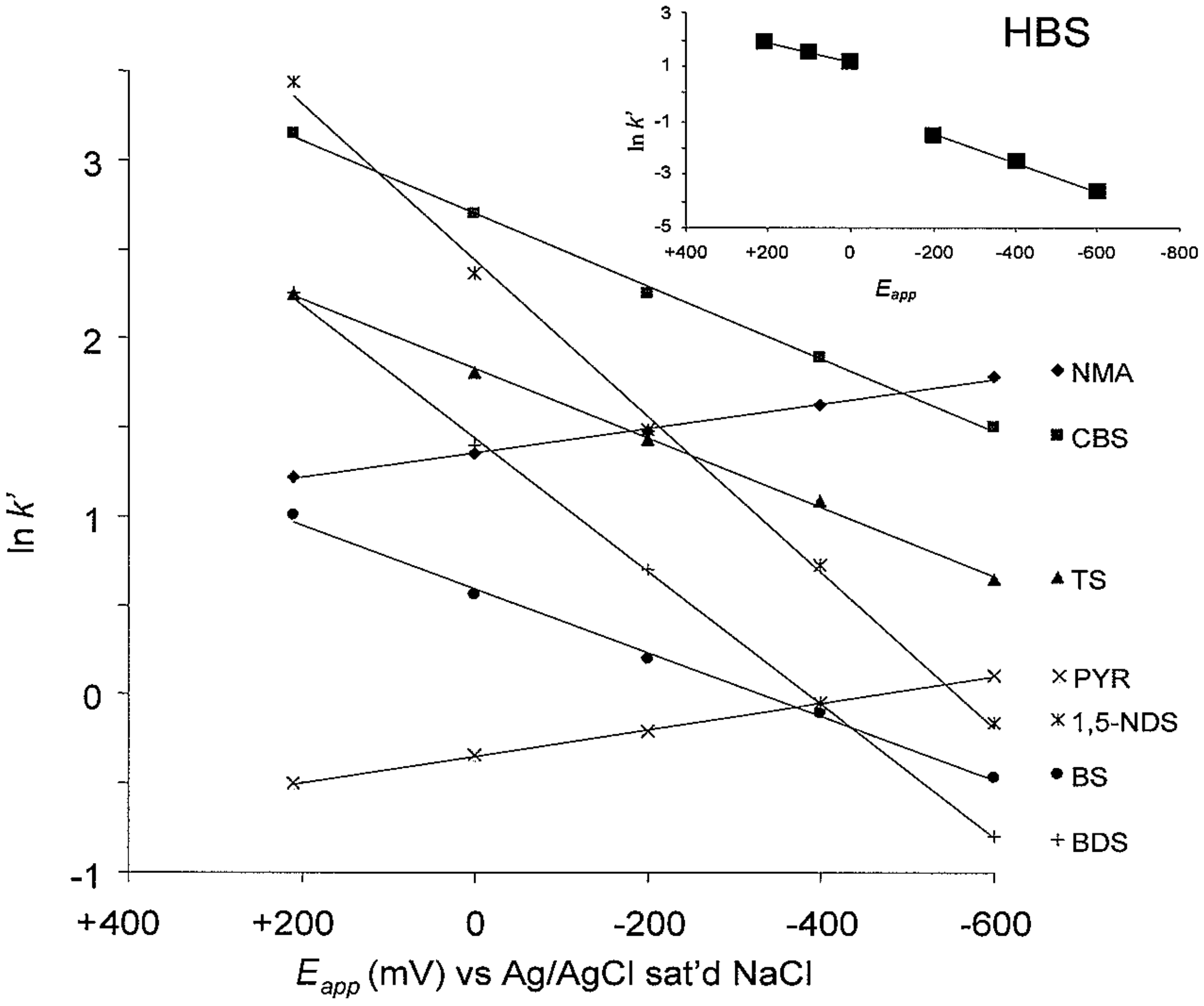


Figure 3. *Plots of log k' versus* E_{app} *for the analytes used in this study. The data points are approximately the size of the error bars from five replicate injections at each* E_{app}. *The mobile phase was composed of 10% acetonitrile in water for BS (10 μM), TS (18 μM), CBS (23 μM) and 1,5-NDS (26 μM); 5% acetonitrile in water with trifluoroacetic acid added to adjust the pH ~ 3 for BDS (13 μM), PYR (31 μM) and NMA (22 μM). Lithium perchlorate (0.1 M) was used as the supporting electrolyte at a flow rate of 0.4 mL/min.*

HBS (Figure 3 inset) suggests anomalous behavior which is attributed to the oxidation of the hydroxyl functional group to a carbonyl group.[3, 34] On either side of this break, the capacity-potential curve is linear, indicating that both redox forms maintain an overall negative charged. However, the offset and change in the slope of the curve indicate that the non-electrostatic component of retention is different for the two forms, reflecting an interplay of the differences in the polarity and hydrophobicity of the two different functional groups. The change in the uv-vis spectral character of the elution band (not shown), which occurs between -100 and -200 mV, supports this claim.

Table1 also shows that the slopes of the capacity-potential curves correlate with the charge of the compound. 1,5-NDS and BDS are divalent anions, CBS, TS, and BS are monovalent anions, and NMA and PYR are monovalent cations. The slopes for 1,5-NDS and BDS in the capacity-potential curve are about twice those for CBS, TS, and BS, which is consistent with the expected differences in electrostatic interactions based on the ionic charge on the two sets of analytes. Moreover, the slopes for NMA and PYR are opposite in sign with respect to those for CBS, TS, and BS. That is, the retention of NMA and PYR undergoes an increase, and not a decrease, in retention as E_{app} moves negatively. This difference also fits with considerations of how E_{app} modulates electrostatic interactions. The two monovalent cations are, however, not as sensitive to changes in E_{app} as the three monovalent anions.

We attribute the difference in the slopes of the monovalent anions and monovalent cations to interactions that act in concert for these anions but are in opposition for these cations. That is, the attraction for positively charged analytes at more negative values of E_{app} is counter-balanced by donor-accepter interactions between the π-systems in the aromatic

Table 1. *ln k' versus* E_{app} *for seven of the test analytes.*

Compound	Ionic Charge	Slope* of ln *k'* vs. E_{app}	R^2
1,5-NDS	-2	-0.0044 ±0.0002	0.9973
BDS	-2	-0.0037 ±0.0005	0.9986
CBS	-1	-0.0020 ±0.0003	0.9973
TS	-1	-0.0019 ±0.0003	0.9986
BS	-1	-0.0018 ±0.0004	0.9963
PYR	+1	+0.0007 ±0.0002	0.9987
NMA	+1	+0.0007 ±0.0002	0.9979

* Standard deviations based on five replicate injections of each sample.

ring of the analyte and the stationary phase. We believe these opposing effects are responsible for variations in the slope of the capacity-potential curve in view of the similarity in the slope for 1,5-NDS and 1,3-BDS, which are divalent anions of different size and charge density. In further support of this argument, the retention of benzene and some of its monosubstituted analogs has been found to decrease as E_{app} is moved to more negative values.[5, 35] The trend in retention for these molecules is like that expected for an anion; a linear capacity-potential curve is observed. In this case, donor-acceptor interactions can be used to explain potential dependent retention of these neutral benzene analogs, in which the change in ln k' with E_{app} would result from electrostatic interactions between the π-systems of the analyte with the stationary phase. The slope for this change was found to be 0.00035 (mV^{-1}) for benzene, a value that is of the same order of magnitude of the slopes for the cations in Table 1. Therefore, if the hetero-aromatic π–systems for the cations in Table 1 behave in a similar fashion, the slopes for the ln k' vs. E_{app} plots would be decreased by an amount related to the strength of these specific donor-acceptor interactions between the analyte and the surface.

In contrast to cations, the interactions between π-systems appear to work in concert with the negative charge of CBS, TS, and BS to enhance the sensitivity of retention with respect to E_{app}. The slopes in the capacity-potential curves for CBS, TS, and BS are indistinguishable even though the absolute values of retention are different, i.e., CBS is the most strongly adsorbed, followed by TS and then BS. However, the comparable dependence of sensitivity to changes in E_{app} indicates that electrostatic interactions play the dominant role in affecting retention rather than on the specific surface-analyte interactions. Although specific surface interactions (e.g., dispersive, hydrophobic, dipole-induced dipole) contribute to the magnitude in which a species adsorbs, the similarities in the slopes between analytes of like charge suggest that changes in $\Delta G_{a\text{-lyte}}$ can be accounted for primarily by electrostatic arguments. The following two sections further investigate this possibility by examining the influence of supporting electrolyte identity and concentration on retention characteristics.

Effect of Supporting Electrolyte Composition

Chromatograms for a series of supporting electrolyte compositions at fixed concentration (0.1 M) are given in Figure 4 with E_{app} equal to +200 mV. The divalent anion BDS and monovalent anion BS served as the analytes. Five different supporting electrolytes were tested: $NaPF_6$, $NaClO_4$, $NaBF_4$, NaOH, and NaF. As shown, changes in the identity of the anion yield significant differences in retention. The use of NaF, for example, resulted in total retention time of ~9 min, whereas that with $NaPF_6$ was less than 2 min. The eluent strength of these anions increases in the order of $F^- < OH^- < BF_4^- < ClO_4^- < PF_6^-$. The differences in the observed eluent strengths suggest that interactions of the supporting electrolyte with the stationary phase beyond only electrostatics must also be considered in the development of a model for the retention mechanism.

In general, the eluotropic order in Figure 4 agrees with electrosorption data obtained on mercury electrodes in which the electrocapillary maximum (ECM) changes with supporting electrolyte composition.[36] Furthermore, these changes in the ECM have been attributed to differing degrees of specific adsorption for the supporting electrolyte on the mercury surface, i.e., $\Delta G_{\text{-e-lyte}}$. There is, however, one notable difference. The ECM for fluoride and hydroxide ions are virtually identical at a mercury electrode where they are both commonly viewed as nonspecific adsorbers. The elution data nevertheless show that NaOH

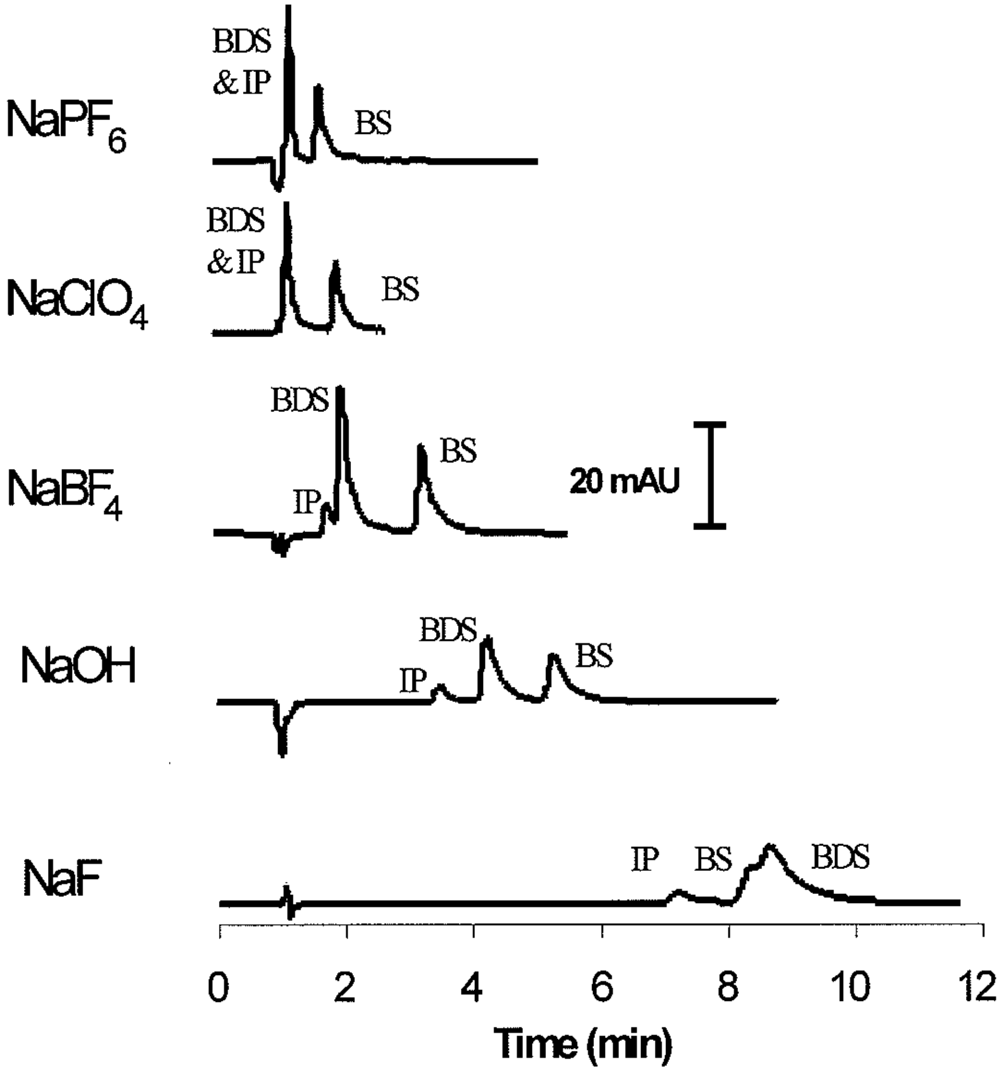


Figure 4 *Chromatograms illustrating the effect of supporting electrolyte identity on the retention of BS (8 μM) and BDS (14 μM) at* $E_{app} = +200$ *mV vs. Ag/AgCl sat'd NaCl. A third peak (IP) is present in each chromatogram which was determined to be a contaminant from the BDS starting material by evaluation of individual injections. The mobile phase consisted of 10% acetonitrile in water with the designated supporting electrolyte present at a concentration of 0.1 M. The flow rate is 0.4 mL/min.*

is a much stronger eluting agent than NaF. This disparity suggests that additional interactions are involved in the adsorption process at the electrified PGC stationary phase.

Contrary to mercury interfaces, carbonaceous materials posses a number of different types of carbon-oxygen surface groups (phenols, lactones, quinones, carboxylic acids, etc...), and differences in solution pH can alter the state of some of these surface groups.[37, 38] For example, when sodium hydroxide is used as the supporting electrolyte, the increase in solution pH may result in deprotonation of oxides on the carbon surface. Deprotonation reactions yield a negatively charged surface oxide which would lower retention of these sulfonates because of electrostatic repulsion. Previous studies have shown that the electrode potential may vary by 20 to 60 mV/pH, leading to a more negative surface potential and may explain the stronger elution strength observed for hydroxide.[39] Taken together, the presence of surface oxides, a potential-pH relationship, and the extent of electrolyte adsorption based on the ECM at mercury are responsible for the general eluotropic trends observed in EMLC.

Effect of supporting electrolyte concentration

The influence of supporting electrolyte concentration (i.e., $LiClO_4$) on the separation of the aromatic sulfonates BS, TS, and CBS is shown by the chromatograms in Figure 5 which were obtained at +200 mV. The elution order (BS < TS < CBS) remained constant at all supporting electrolyte concentrations. Baseline resolution was observed for CBS under all conditions but was lost between BS and TS when the concentration of $LiClO_4$ was greater than 20 mM.

The retention for all three analytes decreased with increasing electrolyte concentration. However, changes in absolute retention times are different for each analyte.

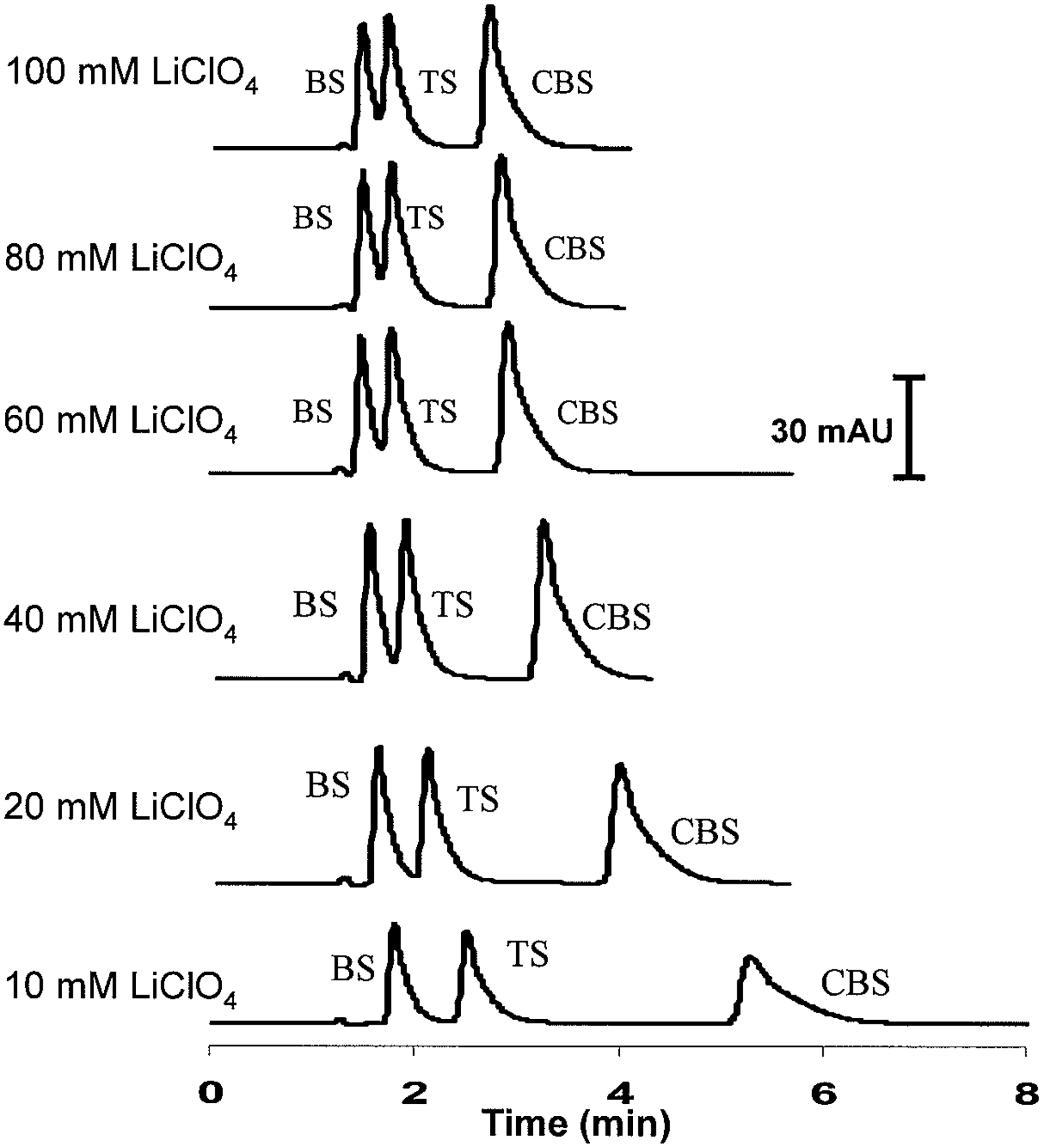


Figure 5. *Chromatograms illustrating the effect of supporting electrolyte concentration on the separation of BS (8 μM), TS (14 μM), and CBS (23 μM). An* E_{app} *of +200 mV vs. Ag/AgCl sat'd NaCl was employed. Mobile phase consisted of 10% acetonitrile in water with the indicated supporting electrolyte concentration. Flow Rate is 0.4 mL/min.*

That is, the most strongly adsorbed analyte (i.e., CBS) is the most affected, whereas the most weakly adsorbed analyte (BS) is the least influenced. For example, *k'* for CBS changes from 3.61 at 10 mM $LiClO_4$ to 1.30 at 100 mM $LiClO_4$, a difference of 2.31. The change in *k'* for BS is much smaller; it goes from 0.57 at 10 mM $LiClO_4$ to 0.23 at 100 mM $LiClO_4$, a difference of only 0.34. The sensitivity for TS, which is intermediate between that for CBS and BS, shows a change in *k'* of 0.80 when comparing 10 mM (k'=1.25) to 100 mM (k'=0.45) $LiClO_4$. The percent decrease in retention that results from the 10-fold increase of $LiClO_4$ concentration was found to be ~60% for each analyte. An electrostatic adsorption model based solely on competition for adsorption sites predicts that a 10-fold increase in electrolyte concentration will reduce analyte retention to 10% of the initial value, a much larger effect than observed.[40] This difference is likely caused by differences in the specific adsorption of the analyte and the electrolyte in that the specific adsorption of the negatively charged analyte is favorable compared to the electrolyte anion. To compensate for specific adsorption effects, the Langmuir adsorption isotherm has been used in conjunction with G-C theory to explain retention in ion-pair chromatography (IPC),[41] and the applicability of this model for EMLC will be discussed shortly.

The potential of zero charge (PZC) of the stationary phase is estimated to be between $-200 < PZC < +100$ mV vs Ag/AgCl saturated NaCl reference, based on reports for various types of carbon electrodes.[42, 43] Therefore, an interfacial excess of electrolyte anions is present under the conditions in Figure 5 since the value of E_{app} is more positive than the expected value for the PZC. From an electrostatic viewpoint, these electrolyte anions would then compete with the negatively charged aromatic sulfonates in counterbalancing the positively charged surface. The excess negative charge adsorbed at the stationary phase will shield analytes in bulk solution from the positively charged surface, thus decreasing the magnitude of electrostatic attraction and decreasing retention. Insights into the type of competition that occurs at the stationary phase, whether specifically for adsorption sites, and/or indirectly through electrostatic interactions may be determined by comparing the experimental data with models that describe the architecture of an electrified interface (see below).

The data in Figure 6 show that a change in supporting electrolyte concentration (0.1 to 0.3 M) has a contrasting effect on the retention of analytes with an opposite charges. The negatively charged TS exhibits a decrease of ~4 min in retention time when lithium perchlorate concentration is increased from 0.1 to 0.3 M. The positively charged PYR, on the other hand, undergoes an increase in retention time of ~4 min for the same change in electrolyte concentration. This difference in behavior argues that a purely competitive mechanism is not always the sole factor responsible for the change in retention. If only a competition mechanism were operative, a decrease in retention for PYR would be expected due to the change in the cation (Li^+) concentration in the mobile phase. The increase in retention for PYR suggests that $\Delta G_{\pm N\text{-}N}$ can also play an important role in dictating EMLC-based retention. Furthermore, the concentration of electrolyte has a strong influence on the electrostatic field experienced by the analyte and may serve to shield the analyte from the stationary phase. Therefore, the basic model of the influence of an electric field on a Boltzmann's distribution of ions that contributes to $\Delta G_{a\text{-}lyte}$ will need to be extended to include the influence of supporting electrolyte concentration on the electric field.

The strong contrast in the behavior of the oppositely charged analytes in Figure 6 can be reasonably explained by the Gouy-Chapman (G-C) theory for the structure of the

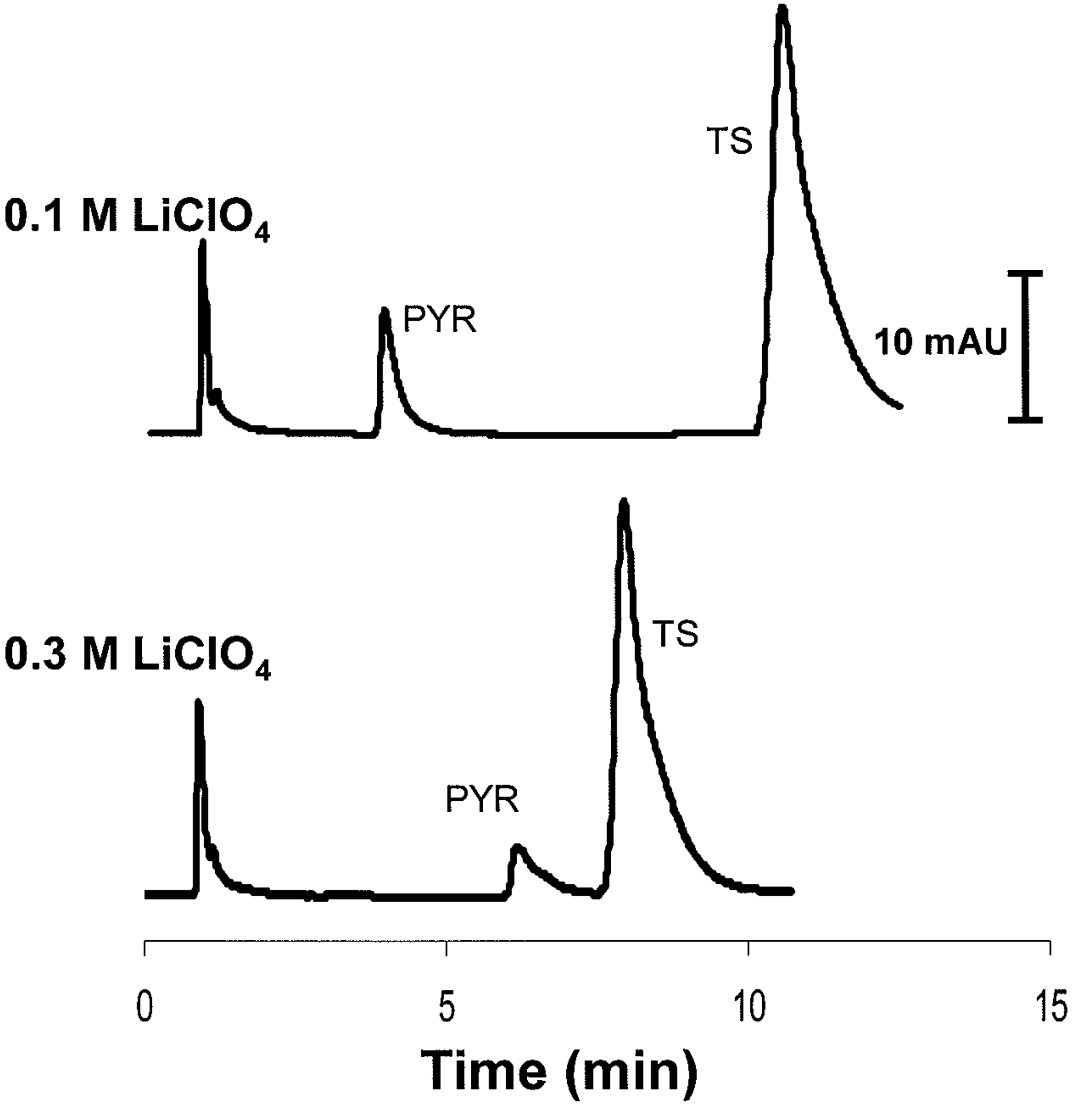
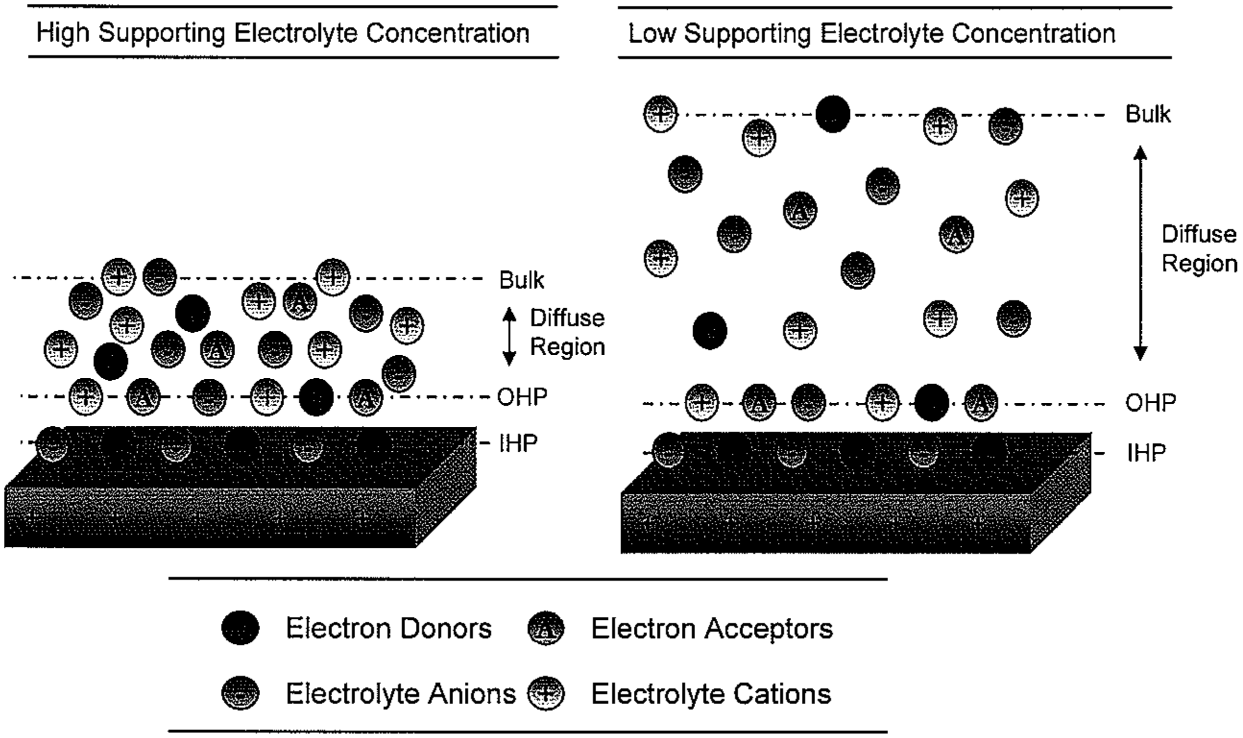


Figure 6 *Effect of supporting electrolyte concentration on the retention of oppositely charged TS (18 μM) and PYR (31 μM). The E_{app} was set to +400 mV vs. Ag/AgCl sat'd NaCl. The mobile phase consists of 10% acetonitrile in water with the indicated supporting electrolyte concentration; TFA was added to mobile phase to adjust the pH ~ 3. The flow Rate is 0.4 mL/min.*



Scheme 2 *Idealized depiction describing the influence of supporting electrolyte on the thickness of the electrical double layer at applied potentials positive of the PZC. These depiction omit contributions from the mobile phase solvent.*

electrical double layer.[40, 44] Scheme 2 illustrates how a change in supporting electrolyte concentration influences the structure of an electrified interface at a positively charged electrode via G-C theory. As shown, G-C theory predicts that an increase in supporting electrolyte concentration will decrease the thickness of the diffuse region of the electrical double layer. Experiments have shown that the diffuse region effectively vanishes at supporting electrolyte concentrations greater than 0.1 M,[36] which results in the accumulation of charge on the solution side of the liquid-solid interface solely at the inner Helmholtz (IHP) and the outer Helmholtz planes (OHP).

At higher supporting electrolyte concentrations, analyte molecules in bulk solution are shielded from the electric field imposed by the potential applied to the stationary phase surface by the counter-ions held in both planes. Shielding by a layer of counter-ions leads to a faster decay of the electrostatic potential on the solution side of the interface, which reduces the extent of electrostatic interactions between the stationary phase and the charged analyte. In other words, the excess of negative charge adsorbed on the stationary phase at more positive E_{app} is strongly influenced by changes in supporting electrolyte concentration, and an analyte at a given distance from the electrode surface would experience greater electrostatic interactions with the stationary phase surface at lower supporting electrolyte concentrations than at higher supporting electrolyte concentration.

The observed behavior can also be explained by an ion-pairing phenomenon in which the analyte electrostatically interacts with ions in the double layer at the surface. At potentials positive of the PZC, the double layer consists of an excess of anions. Since higher concentrations of supporting electrolyte would confine drops in potential to primarily the IHP and OHP, cationic analytes would be attracted while anionic analytes would be repelled by this compact layer of anions. The next section examines these data within the context of a mathematical model of retention in EMLC.

Modeling EMLC

These data indicate that $\Delta G_{a\text{-lyte}}$, $\Delta G_{\pm e\text{-lyte}}$, and $\Delta G_{\pm N\text{-}N}$ play a more prominent role in retention than $\Delta G_{\pm int}$. Again, $\Delta G_{\pm e\text{-lyte}}$ and $\Delta G_{\pm N\text{-}N}$ describe the competition between electrolyte and analyte for stationary phase surface sites, while $\Delta G_{a\text{-lyte}}$ describes the direct interaction between the analyte and the stationary phase. Since $\Delta G_{\pm e\text{-lyte}}$ changes with E_{app}, the competition for adsorption sites would be potential dependent and is the most likely origin for the nonlinear behavior observed for some analytes in EMLC. Furthermore, $\Delta G_{a\text{-lyte}}$ can be dissected into electrostatic and non-electrostatic components, where supporting electrolyte concentration can modulate the electrostatic component as well as the available number of adsorption sites. The influence of supporting electrolyte concentration on the electrostatic component of retention will be described first using using classical G-C theory. The use of a Langmuir adsorption isotherm to describe the influence of electrolyte concentration on non-electrostatic component (i.e., specific adsorption of electrolyte) will ensue through comparisons of IPC models that use this type of methodology as applied to EMLC data.

The relationship between the charge on the electrode surface, potential, and supporting electrolyte concentration in the GC theory for a 1:1 supporting electrolyte is given by[44, 45]

$$q_{\pm sol} = \sqrt{\frac{\varepsilon C_M kT}{2\pi}}\left(e^{-z_\pm e_0 \Psi / 2kT} - 1\right) \qquad (1)$$

where $q_{\pm sol}$ is the excess interfacial charge on the solution side of the interface, ε is the dielectric constant of solvent in the interphase, C_M is the bulk concentration of supporting electrolyte, k is Boltzmann constant, T is the temperature in Kelvin, z_i is the valence of species i, e_0 is the electronic charge, and Ψ is the surface potential. The modification of Equation 1 to describe the capacity factor, k' as a function of potential and concentration of supporting electrolyte is presented in Appendix 1 and the result is given by Equation 2.

$$k' = \frac{A}{V_M \kappa}\left(e^{-ze_0\Psi/kt} - 1\right) + 1 \qquad (2) \qquad \kappa^{-1} = \left(\frac{\varepsilon kT}{2\pi (zF)^2 C_M}\right)^{1/2} \qquad (3)$$

where A is the surface area of the stationary phase, V_m is the volume of the mobile phase, and the Debye length, κ^{-1}, is defined in Equation 3. The other terms have the same meaning as before.

Equation 2 predicts that *k'* is inversely dependent on the square root of the supporting electrolyte concentration, and plots of this relationship are shown for the three different analytes in Figure 7 at several values of E_{app}. Importantly, *k'* for all analytes becomes more sensitive to changes in supporting electrolyte concentration as the value of E_{app} becomes more positive. These findings are consistent with the predictions of Equation 2. For example, when E_{app} >> PZC the parenthetical term in Equation 2, $(e^{-ze\Psi/kt}-1)$ is greater than zero for a negatively charged analyte. An increase in supporting electrolyte concentration would therefore decrease retention. This expectation is met for all three analytes.

The behavior of cationic PYR observed in Figure 6 can also be predicted by Equation 2. That is, at E_{app} >> PZC the parenthetical term in Equation 2 is less than zero for a cation, and the observed increase in retention is predicted as the supporting electrolyte concentration increases. Another interesting observation develops as E_{app} approaches the

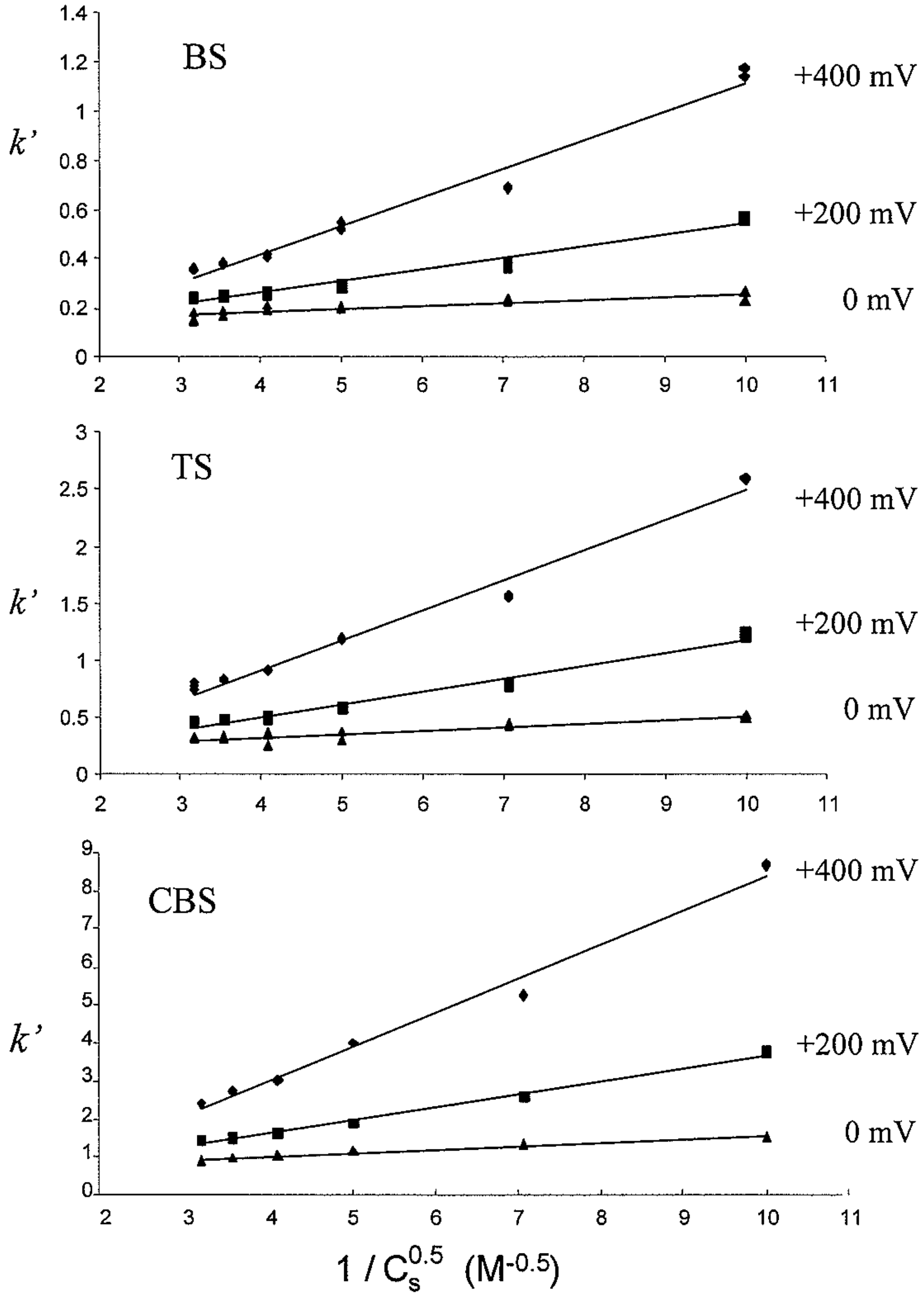


Figure 7. *A plot of k' versus* $1/\sqrt{F}$ *for BS (8 μM), TS (14 μM), and CBS (23 μM). Three replicate injections were made at each concentration studied, and the data points are roughly the size of the error bars. The mobile phase consisted of 10% acetonitrile in water using sodium fluoride as the supporting electrolyte at concentrations of 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 M.*

PZC. As E_{app} moves closer to the PZC, the parenthetical term in Equation 2 approaches zero. That is, analyte retention becomes independent of supporting electrolyte concentration at the PZC. Examination of Equation 2 at the PZC states that k' is equal to one, indicating that the electrostatic component of retention is of little influence at the PZC where retention would be governed only by specific interactions with the surface. Furthermore, the consistency between the data and predictions made by G-C theory suggests that such studies may provide a means to determine the PZC of EMLC stationary phases.

The use of G-C theory to explain chromatographic retention is not unique to EMLC. As previously mentioned, G-C theory has been applied extensively to mechanistic treatments of ion-pair chromatography (IPC).[41, 46] There are two prevailing models that draw on G-C theory as a basis for a description of the fundamental role of interfacial potential in IPC: the Stahlberg[47] model and the Cantwell[48] model. Both models follow the key assumptions of G-C theory: 1) the electrode surface is impenetrable for electrolyte ions; 2) the charge on the electrode is uniformly spread over its surface; 3) electrolyte ions behave as point charges; and 4) the dielectric constant of the solvent is independent of distance from the electrode surface. These assumptions are equally applicable to EMLC, where the surface charge density, $\sigma_{\pm}$, stems from the potential applied to the polarizable stationary-mobile phase interface. However, $\sigma_{\pm}$ in IPC is determined by the concentration of charged functional groups attached to the surface of the stationary phase and by the concentration of the pairing ion. The diffuse structure of the electrical double layer is assumed to start at the electrode surface in the Stahlberg model. On the other hand, the model by Cantwell invokes the Stern modification in which the diffuse part of the electrical double layer begins after the compact layer. The Cantwell model further assumes that only the analyte can contact adsorb onto the stationary phase surface and that for each charged analyte that enters the diffuse portion of the electrical double layer a similarly charged electrolyte ion leaves the diffuse double layer region, i.e., an ion-exchange process. The Stahlberg model, however, accounts for the contact adsorption of both analyte as well as the supporting electrolyte through the use of a modified Langmuir adsorption isotherm.

Both models therefore invoke G-C theory to describe the electrostatic interactions of relevance to IPC, but differ in how the direct competition for adsorption sites on the stationary phase occurs. The Stahlberg model predicts that a plot of log k' vs. log C_s would be linear, a relationship often observed in IPC, which is functionally identical to the logarithmic form of Equation 2. The Cantwell model, on the other hand, predicts an inverse relationship between k' and supporting electrolyte concentration due to competition for adsorption sites on the surface.

To ascertain which model is best suited for interpreting EMLC data, R^2 values from a regression analysis for plots of k' versus $1/C_s$ given by Cantwell, log k' versus log C_s as modeled by Stahlberg, and k' versus $1/\sqrt{C_s}$ relationship represented by Equation 2 (EDL) are provided in Table 2. While mathematically similar, the Stahlberg model only differs from Equation 2 through an additional term that employs a potential dependent Langmuir adsorption isotherm to describe the extent of contact adsorption on the surface. As mentioned, the changes in the slope at different values of E_{app} for each type of plot can be predicted by double layer theory, and Table 2 suggests that the effectiveness of these models to describe EMLC retention is also potential dependant. For example, when sodium fluoride is the supporting electrolyte, these models appear less effective at -50 mV with respect to the other values of E_{app}. Lithium perchlorate shows a similar deficiency at -300 mV.

Table 2 *Correlation analysis of possible models with experimental data. R^2 values taken from plots of k' versus 1/C (Cantwell), log k' versus log C (Stahlberg), and k' versus $C^{-1/2}$ (EDL). Plots generated from chromatographic separations performed on a mixture of aromatic sulfonates at multiple concentrations of NaF or $LiClO_4$ for each value of E_{app}. Each entry is the average of five replicate injections.*

Analyte	E_{app}	Cantwell (NaF)	Stahlberg (NaF)	EDL (NaF)	Cantwell ($LiClO_4$)	Stahlberg ($LiClO_4$)	EDL ($LiClO_4$)
TS	+50 mV	0.9846	0.9980	0.9985	---	---	---
TS	0 mV	0.9623	0.9803	0.9979	0.9514	0.9567	0.9628
TS	-50 mV	0.7408	0.7826	0.7685	0.9538	0.9128	0.9560
TS	-100 mV	0.9627	0.9990	0.9881	0.9542	0.9215	0.9557
TS	-150 mV	0.9863	0.9872	0.9973	0.9160	0.9671	0.9586
TS	-200 mV	---	---	---	0.9440	0.8813	0.9514
TS	-300 mV	---	---	---	0.6748	0.8675	0.8884
TS	-400 mV	---	---	---	0.9490	0.9358	0.9154
	avg	0.9273	0.9494	0.9501	0.9062	0.9204	0.9412
BS	+50 mV	0.9551	0.9970	0.9836	---	---	---
BS	0 mV	0.9584	0.9969	0.9851	0.9371	0.9610	0.9560
BS	-50 mV	0.6602	0.6958	0.7093	0.9605	0.9354	0.9552
BS	-100 mV	0.9680	0.9958	0.9891	0.8776	0.9477	0.9186
BS	-150 mV	0.9744	0.9974	0.9943	0.8849	0.9416	0.8925
BS	-200 mV	---	---	---	0.9121	0.9275	0.9018
BS	-300 mV	---	---	---	0.6143	0.7431	0.7675
BS	-400 mV	---	---	---	0.8654	0.9505	0.9696
	avg	0.9032	0.9366	0.9323	0.8646	0.9153	0.9087
CBS	+50 mV	0.9431	0.9906	0.9746	---	---	---
CBS	0 mV	0.9759	0.9982	0.9946	0.9477	0.9645	0.9628
CBS	-50 mV	0.9227	0.9735	0.9440	0.9682	0.9349	0.9560
CBS	-100 mV	0.9858	0.9899	0.9975	0.9442	0.9504	0.9357
CBS	-150 mV	0.9600	0.9984	0.9859	0.9666	0.9254	0.9301
CBS	-200 mV	---	---	---	0.9597	0.9448	0.9386
CBS	-300 mV	---	---	---	0.7068	0.8244	0.7984
CBS	-400 mV	---	---	---	0.8768	0.8499	0.8234
	avg	0.9575	0.9901	0.9793	0.9100	0.9135	0.9064
1,3-BDS	+50 mV	0.9574	0.9626	0.9674	---	---	---
1,3-BDS	0 mV	0.9190	0.9700	0.9550	0.9330	0.9671	0.9578
1,3-BDS	-50 mV	0.6694	0.6091	0.6983	0.8739	0.9371	0.9156
1,3-BDS	-100 mV	0.8742	0.9650	0.9209	0.8985	0.9468	0.9318
1,3-BDS	-150 mV	0.7895	0.9252	0.9545	0.8968	0.9531	0.9343
1,3-BDS	-200 mV	---	---	---	0.9658	0.9547	0.9043
1,3-BDS	-300 mV	---	---	---	0.7058	0.7750	0.7423
1,3-BDS	-400 mV	---	---	---	0.9210	0.9389	0.9366
	avg	0.8419	0.8864	0.8992	0.8850	0.9247	0.9032
1,5-NDS	+50 mV	0.8962	0.9690	0.9742	---	---	---
1,5-NDS	0 mV	0.9616	0.9511	0.9627	0.9550	0.9695	0.9576
1,5-NDS	-50 mV	0.5843	0.6134	0.6785	0.9679	0.9359	0.9484
1,5-NDS	-100 mV	0.9720	0.9912	0.9904	0.7460	0.8301	0.8908
1,5-NDS	-150 mV	0.8542	0.9532	0.9906	0.8936	0.8922	0.9257
1,5-NDS	-200 mV	---	---	---	0.9190	0.8828	0.8764
1,5-NDS	-300 mV	---	---	---	0.7071	0.7949	0.7689
1,5-NDS	-400 mV	---	---	---	0.9355	0.9306	0.9279
	avg	0.8537	0.8956	0.9193	0.8749	0.8909	0.8994
	tot avg:	0.8967	0.9316	0.9360	0.8881	0.9129	0.9118

Cantwell average:	0.8924
Stahlberg average	0.9223
EDL average	0.9239

Interestingly, the values of E_{app} with the poorest agreement for all three models correspond closely to the values that we have determined from a thermodynamic treatment of EMLC data that will soon be reported elsewhere.[49]

The utility of these models to predict the electrolyte concentration dependence of retention is consistent with expectations. That is, the contribution of electrostatic and ion-exchange processes to retention is at a minimum at the PZC, suggesting that the predominant retention mechanism would be different at the PZC than at potentials removed from the PZC. Furthermore, retention at the PZC should at least qualitatively correlate with reversed phase behavior, which is consistent with the observed hydrophobic contribution to retention that is observed at carbonaceous stationary phases.[24]

Table 2 also argues that all three mechanisms reasonably describe the dependence of analyte retention on E_{app} at values removed from the PZC, although the Stahlberg and the EDL models show the strongest correlations. In other words, while the contribution to the total charge in the diffuse region is satisfied by a competition between analyte and supporting electrolyte, as all models indicate, the additional assumptions incorporated to account for ion-pairing are of clear importance. The lower correlation with the Cantwell model suggests that the assumed ion-exchange process occurring in the diffuse region is not central in determining retention in EMLC. While it may be a coincidence, Table 2 suggests that, on average, the EDL model is somewhat more predictive with NaF as the supporting electrolyte, whereas the Stahlberg model is a little more reliable when $LiClO_4$ is used.

Fluoride is typically viewed as a weak specific adsorbent on electrodes, signifying a small $\Delta G_{e\text{-}lyte}$. This situation suggests that the predominant competition between fluoride and the analyte occurs in the diffuse double layer. Experiments using perchlorate as the supporting electrolyte show that Stahlberg's model is slightly more accurate, indicating that the competition for adsorption sites is more important with this electrolyte anion and is consistent with its stronger eluent strength. Taken together, these results suggest that the retention mechanism changes from an ion-exchange model at more extreme potentials to a reverse phase model near the PZC.

Use of Supporting Electrolyte in EMLC

Finally, Figure 8 presents a preliminary indication of how supporting electrolyte concentration can be used to manipulate EMLC separations. Chromatogram 8A shows the separation of a mixture of BS, TS, NMA, and CBS with 0.1 M $LiClO_4$ used as the supporting electrolyte throughout the elution process. Under these conditions, baseline resolution of BS and CBS was obtained, but the oppositely charged TS and NMA were found to co-elute. The results reported in the preceding sections suggest two possible ways to resolve the co-eluents: a change in E_{app}, as hinted at in Figure 3, or a change in supporting electrolyte concentration, as suggested by Figures 5 and 6. The application of a concentration gradient would be particularly attractive to instances in which the electroactivity of one or more of the components in a sample would possibly preclude the use of a change in E_{app} to fine-tune the separation. For example, a compound may be transformed into a range of products by follow-up chemical reactions. It is also possible that a redox reaction may yield an undetectable product. A concentration gradient would therefore modulate the potential profile at the interface and avoid a change in the redox state of the sample constituents.

In an attempt to resolve TS and NMA by changing the supporting electrolyte concentration, two different stepwise gradients in the concentration of $LiClO_4$ were tested.

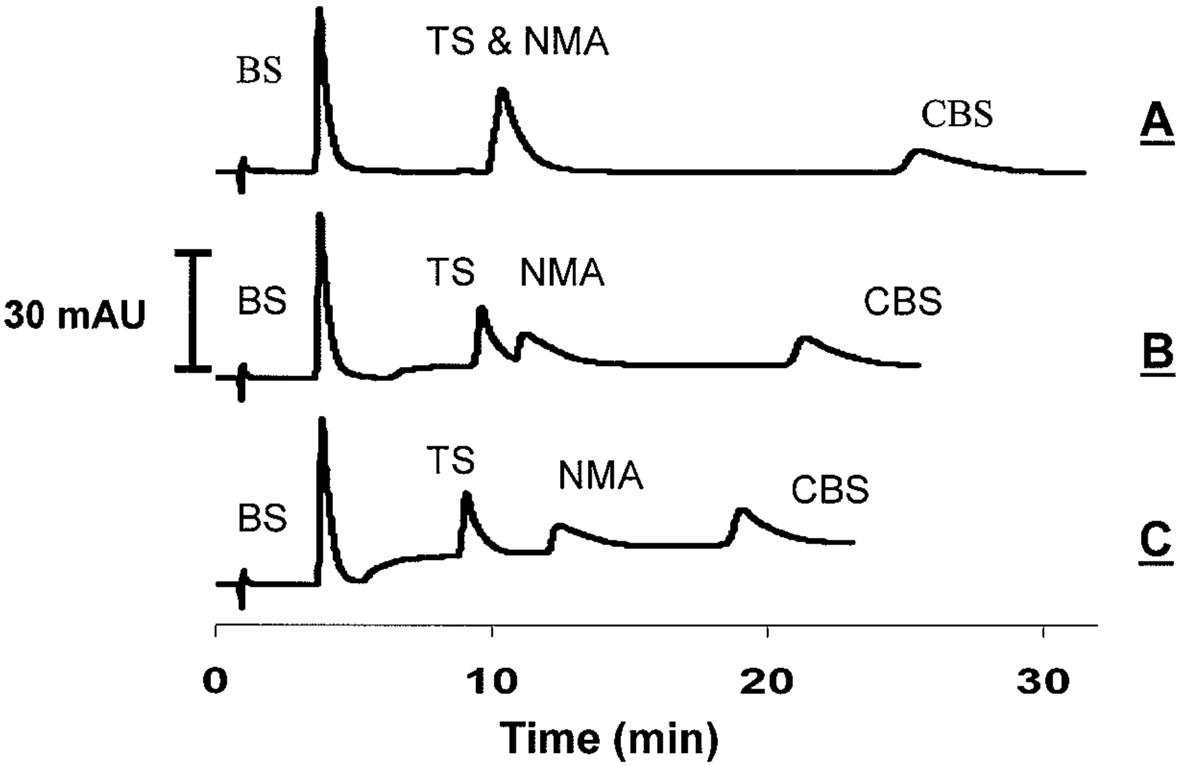


Figure 8. *Chromatograms that illustrate the utility of a supporting electrolyte concentration gradient for the enhancement of EMLC separations. The sample mixture was composed of BS (8 μM), TS (14 μM), CBS (23 μM), and NMA (22 μM). The mobile phase consisted of 5% acetonitrile in water with TFA added to adjust the solution pH to ~2. The absorbance at 212 nm was monitored. The flow rate was set at 0.4 mL/min. The applied potential is +400 mV vs. Ag/AgCl sat'd NaCl.*

Table 3 *The supporting electrolyte concentration gradient used to generate the corresponding chromatograms in Figure 8.*

Time (min)	*0-5*	*5-18*	*18-*
A	0.1 M $LiClO_4$	0.1 M $LiClO_4$	0.1 M $LiClO_4$
B	0.1 M $LiClO_4$	0.2M $LiClO_4$	0.2 M $LiClO_4$
C	0.1 M $LiClO_4$	0.3 M $LiClO_4$	0.4 M $LiClO_4$

These results are presented in chromatograms 8B and 8C. In chromatogram 8B, the electrolyte was held at 0.1 M $LiClO_4$ for 5 min after injection and then was stepped to 0.2 M. In chromatogram 8C, the electrolyte was again held at 0.1 M $LiClO_4$ for 5 min after injection before being stepped to 0.3 M. The changes in the baseline observed in both chromatograms are due to the changes in supporting electrolyte concentration, reflecting the absorption of perchlorate ion at the wavelength (212 nm) used for detection. Partial resolution of TS and NMA is obtained when the supporting electrolyte concentration was increased as in chromatogram 8B. Baseline resolution was achieved using the larger stepwise concentration gradient that was employed in chromatogram 8C. These results show that changes in the supporting electrolyte concentration alter the selectivity of an EMLC column, and are consistent with the discussions based on the data in Figures 2-7.

Figure 8 also demonstrates that altering the concentration of supporting electrolyte can be used to optimize the analysis time. The retention time of CBS was decreased by ~10 min in moving from the isocratic separation in chromatogram 8A to the stepwise electrolyte concentration gradient used in chromatogram 8C.

CONCLUSION

This paper has examined the influence of supporting electrolyte on the retention of charged analyte molecules in EMLC. Both direct and indirect competition for adsorption sites onto the stationary phase surface were found to strongly affect retention. Direct competition for occupancy of adsorption sites on the stationary phase is expressed as a combination of $\Delta G_{\pm e\text{-lyte}} + \Delta G_{\pm N\text{-}N}$, which influence retention most strongly with changes in the identity of the supporting electrolyte. The inclusion of direct competition into the retention mechanism for EMLC to describe changes in supporting electrolyte identity requires information about the total free energy of adsorption for the supporting electrolyte itself. Indirect competition may be explained as a modulation of the electrostatic potential profile component of $\Delta G_{a\text{-lyte}}$, and was found to be a significant factor towards changes in analyte retention as a function of supporting electrolyte concentration. Furthermore, the influence of supporting electrolyte concentration was found to depend on the charge of the analyte and the potential applied to an EMLC column. This behavior can be explained by a shielding of electrostatic analyte-stationary phase interactions via a change in the potential profile as a function of distance from the electrode surface, as calculated from electrical double layer theory. Furthermore, the use of Gouy-Chapman-Stern diffuse double layer in future experiments may prove valuable in determining fundamental electrochemical properties of the stationary-mobile phase interface in EMLC such as the PZC and electrical capacitance of our columns.

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APPENDIX

Relationship between Gouy-Chapman theory and chromatographic retention

The relationship between charge in solution, potential applied to an electrode, and distance from the electrode surface for a 1:1 supporting electrolyte according to Gouy Chapman theory was given by Equation 1. When the potential applied to the electrode is negative of the PZC, Equation 1 yields the value of q_{+sol}, while at positive potentials versus the PZC Equation 1 provides the value for q_{-sol}. The charge in solution at the electrified interface is directly related to the surface excess of ions through the following relationship:

$$q_{\pm} = zF\Gamma_{\pm} \qquad (A-1)$$

where $\Gamma_{\pm}$ is the surface excess of either the cations (+) or anions (-) at the electrified interface. For the situation when the applied potential is positive of the PZC, Equation A-1 can be inserted into Equation 1 to give:

$$zF\Gamma_{-} = \sqrt{\frac{\varepsilon C_M kT}{2\pi}}\left(e^{-z_{-}e_0\Psi_0/2kT} - 1\right) \qquad (A-2)$$

The surface excess describes adsorption of a given ion at the interface, and is related to the capacity factor (*k'*) that is determined chromatographically. In other words, Γ describes the difference between the amount of a given species at the interface, n_s, and that in the bulk solution, n_M, after normalization for the area of the interface. Equation A-3 presents the formal definition of Γ_-..On the other hand, *k'* describes the ratio of absolute amounts of a species adsorbed on the stationary phase and in the mobile phase as shown in Equation A-4.

$$\Gamma_- = \frac{1}{A}\left(n_S - n_M\right) \qquad (A-3)$$

$$k' = \frac{C_S V_S}{C_M V_M} = \frac{n_S}{n_M} \qquad (A-4)$$

Where C_S and C_M are the surface and bulk solution concentrations, respectively, and V_S and V_M are the stationary phase and mobile phase volumes, respectively. By substitution $n_M k'$ in Equation A-4 for the n_S term in Equation A-3, the relationship between capacity factor and surface excess can be determined:

$$\Gamma_- = \frac{n_M}{A}\left(k' - 1\right) \qquad (A-5)$$

Substitution of Equation A-5 into Equation A-2 shows the relationship between *k'* and potential at the interface as modified by supporting electrolyte concentration:

$$\frac{zFn_M}{A}\left(k' - 1\right) = \sqrt{\frac{\varepsilon C_M kT}{2\pi}}\left(e^{-z_- e_0 \Psi_0 / 2kT} - 1\right) \qquad (A-6)$$

Rearrangement of (7) and using the relationship of $n_M = C_M V_M$ from (5) gives:

$$\left(k' - 1\right) = \frac{A}{V_M}\sqrt{\frac{\varepsilon kT}{2\pi (zF)^2 C_M}}\left(e^{-z_- e_0 \Psi_0 / 2kT} - 1\right) \qquad (A-7)$$

The square root term in Equation A-7 is the Debye length, κ^{-1}, which characterizes the distance between two plates of a parallel plate capacitor that would mimic the real situation occuring in solution. Substitution of κ^{-1} into Equation A-7 and adding one to both sides then gives Equation 2, which was presented in an earlier section. This relationship describes the influence of potential and supporting electrolyte concentration on the capacity factor of an ionic species based solely on electrostatic interactions.

CHAPTER 3. ELECTROCHEMICALLY MODULATED LIQUID CHROMATOGRAPHY AND THE GIBBS ADSORPTION EQUATION

A paper to be submitted to *The Journal of the American Chemical Society*

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ABSTRACT

This paper examines retention at an electrified porous graphitic carbon stationary phase as monitored by electrochemically modulated liquid chromatography (EMLC) and dissected through considerations of the Gibbs adsorption equation. EMLC employs a conductive material as both a stationary phase for chromatographic separations and as a working electrode for electrifying the stationary phase. This dual functionality gives EMLC the capacity to manipulate chromatographic separations by changing the potential applied (E_{app}) to the stationary phase. The ability to monitor retention as a function of E_{app} provides a means to chromatographically monitor electrosorption processes at solid-liquid interfaces.

From the chromatographic data, it is possible to determine the interfacial excess (Γ) of a solute and changes in interfacial tension ($d\gamma$) as a function of both E_{app} and the supporting electrolyte concentration. Taken together, these two experimentally manipulated parameters can be examined within the context of the Gibbs adsorption equation to delineate the contribution of a variety of interfacial properties, including the charge of solute on the

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stationary phase and the potential of zero charge (PZC), to the mechanism behind EMLC-based retention. This paper examines the influence of the identity and concentration of several supporting electrolytes (sodium fluoride, lithium perchlorate, and potassium chloride) and E_{app} on Γ for several charged aromatic sulfonates. A chromatographic procedure for PZC determination is presented via capacity-potential curves by monitoring the electrosorption of charged eluites, as is a means to quantify the extent of specific adsorption and eluent strength of supporting electrolyte.

INTRODUCTION

Electrochemically modulated liquid chromatography (EMLC) is a unique combination of high performance liquid chromatography (HPLC) and electrochemistry. EMLC employs a conductive material as both the stationary phase for HPLC experiments and as the working electrode in a three-electrode electrochemical cell. By changes in the electrical potential of the conductive stationary phase, the retention of a solute can be manipulated as a consequence of alterations in electrosorption processes. To date, most of the research in EMLC has focused on its ability to enhance separations and on changes in column design for improvement of both chromatographic and electrochemical performance.[1-11] The work herein takes a different tactic by viewing EMLC as a tool for the examination of fundamental properties of electrified solid-liquid interfaces. As will be shown, the chromatographic component of EMLC can be applied to the direct determination of eluite adsorption because of the relationship between the migration rate and the partition coefficient of an eluite and the linear velocity of the mobile phase. The electrochemical component of EMLC, on the other hand, permits an investigation of the relationship between the migration rate of an eluite and the potential applied to the stationary phase (E_{app}). By combining these characteristics, EMLC-based retention data can yield intriguing insights into how E_{app} modifies the extent of eluite adsorption onto the stationary phase.

Various factors that influence changes in retention as a function of E_{app} in EMLC have recently been reviewed.[12, 13] In short, Nernstian behavior has been employed to describe potential-induced changes in retention through the redox activity either of an electroactive analyte, of mobile phase components, or of polymeric coatings on the stationary phase surface.[4, 14-17] For electrochemically inert systems, electron donor-acceptor interactions can be used to qualitatively assess the relationship between the capacity factor (k') of a charged eluite (e.g., aromatic sulfonates, protonated pyridines, and inorganic anions) and E_{app}.[6, 13, 18-20] These systems yield trends that are consistent with theoretical predictions based on the influence of an electric field on a Boltzmann's distribution of ions.

Experimental evidence to date, however, shows that these models can be ineffective in explaining several of the observed trends such as the potential dependent retention of neutral molecules, mandating further investigation. Furthermore, recent work has shown that changes in E_{app} alter the interactions with the stationary phase within the context of the submolecular electronic, steric, and hydrophobic parameters of the analyte.[5, 10] In order to accurately delineate the role of these interactions, shifts in the chemical equilibrium that arise due to potential dependent adsorption of the solvent and any mobile phase additives (supporting electrolyte, organic modifiers, pH buffers, etc.) must be considered in greater detail.

This paper is part of a series of investigations that examines these effects through modeling of the interface via Gouy-Chapman electrical double layer,[21] and by theoretical work in the thermodynamics involved in adsorption at interfaces.[22] The success of these approaches in describing the electrostatic aspects of EMLC retention suggests a close similarity between the energetics of retention in EMLC with those observed in traditional electrochemical cells insomuch as the thermodynamic relationships developed in investigating these traditional systems may also be applied to EMLC. By monitoring the surface excess as a function of E_{app} and mobile phase composition at constant temperature and flow, this paper investigates the ability of interfacial thermodynamics to delineate key factors of the electrified interface that contribute to EMLC-based retention.

Theoretical Background

Application of the Gibbs adsorption equation to EMLC permits first principle assessments of the thermodynamics that govern eluite retention. The historic use of this equation rests with its description of potential dependence of adsorption via electrocapillary experiments, and has been extensively reviewed.[23-27] In the classical treatment, the system consists of an electrolyte solution, the electrodes, and a potentiostat. The interfacial tension of a hanging drop mercury electrode was determined as a function of potential and solvent composition through measures that detected changes in droplet size and shape. These results were used to calculate key descriptors of the electrified interface, most notably the electrode charge and several different types of interfacial excesses. By assuming an ideally polarized mercury-solution interface and the absence of junction potentials throughout the rest of the cell and by applying the Gibbs-Duhem relationship, a specific, yet simple form of the Gibbs adsorption relationship can be derived and is given in Equation 1.

$$(1)\quad -d\gamma = q^{M}\, dE_{app} + \sum_{i} \Gamma_{i} du_{i}$$

In this equation, γ is the interfacial tension, q^M is the charge on the electrode, and Γ_i and $d\mu_i$ are the respective surface excesses and chemical potentials associated with all ions *i* present in solution. When the composition of the solution is held constant, Equation 1 can be differentiated to give Equation 2, the Lippmann equation.

$$(2)\quad \left[\frac{-d\gamma}{dE_{app}}\right]_{u_i} = q^{M}$$

The Lippmann equation states that the sensitivity of interfacial tension toward changes in E_{app} can be used to determine q^M. In addition to the Lippmann equation, the classical form of the Gibbs adsorption isotherm can be obtained through differentiation of Equation 1 at a fixed value of E_{app}, yielding Equation 3.

$$(3)\quad \left[\frac{-d\gamma}{du_i}\right]_{E_{app}} = \Gamma_{i}$$

The Gibbs adsorption isotherm is therefore useful for the determination of interfacial excesses of the constituent components of the electrolyte which is a direct measure of the extent of constituent adsorption.

Electrosorption at solid-liquid interfaces can be interrogated by a variety of techniques,[28] and by taking advantage of the ability to monitor the potential dependence of the retention of a solute on a stationary phase, EMLC adds to this repertoire. Importantly, the interfacial excess that is part of the above equations is closely related to the chromatographic capacity factor of eluite i (k'_i) that is experimentally determined by EMLC.

As defined in Equation 4, k'_i describes the migration rate of solute i in a column as a function of its distribution between the mobile and stationary phases.

$$(4)\quad k'_i = \frac{n_s}{n_m}$$

In Equation 4, n_s and n_m represent the amount of solute adsorbed onto the stationary phase and the number of solute molecules in bulk solution, respectively. Similarly, Γ_i is defined in Equation 5 as the difference in concentration of a species present in the interfacial region and its concentration in bulk solution.

$$(5)\quad \Gamma_i = \frac{1}{A}\left(n_s - n_m\right)$$

Realizing that total amount of analyte is fixed by the volume and concentration of sample injected onto the column, the relationship between k'_i and Γ_i is described in Equation 6 by combining Equations 4 and 5,

$$(6)\quad \Gamma_i = \frac{n_{tot}}{A}\frac{\left(k'_i - 1\right)}{\left(k'_i + 1\right)}$$

where A is the surface area of the stationary phase, and n_{tot} is the total number of analyte molecules injected onto the column. Taken together, Equations (1) through (6) permit the calculation of q^M, Γ_i and $d\gamma$ from the experimentally observed values of k'_i. That is, Γ_i can be determined based on the retention of a sample of known composition, and subsequently used to calculate its contribution to the charge on the stationary phase and changes in interfacial tension.

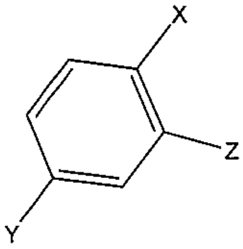
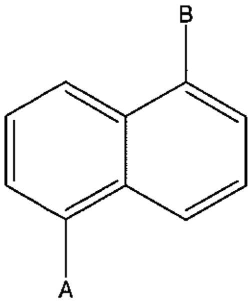
EXPERIMENTAL SECTION

Chemicals and Reagents

The structures of the analytes, along with their acronyms are given in Table 1. Disodium 1,3-benzenedisulfonate (BDS), sodium benzenesulfonate (BS), sodium para-toluenesulfonate (TS), phenyltrimethlyammonium para-toluenesulfonate (PTMA-TS), dibromomethane and lithium perchlorate were purchased from Aldrich (Milwaukee, WI, USA). Sodium para-chlorobenzenesulfonate (CBS) was obtained from TCI America (Portland, OR, USA). Disodium 1,5-naphthalenedisulfonate (1,5-NDS) was acquired from Eastman Kodak (Rochester, NY, USA). Acetonitrile, sodium fluoride and potassium chloride were purchased from Fisher Scientific (Fair Lawn, NJ, USA). All chemicals were used as received, and all aqueous solutions were prepared with water purified by a Millipore Milli-Q system (Bedford, MA, USA). Before use, the solutions were filtered through a 0.5-μm filter (Osmonics, Minnetonka, MN, USA), and thoroughly degassed by sparging with helium.

The experiments employed 5-*μ*m Porous Graphitic Carbon (PGC; ThermoHypersil, Bellefonte, PA, USA) particles as the stationary phase. As-received PGC has been characterized by X-ray photoelectron spectroscopy as devoid of any detectable oxygen-containing functional groups (estimated detection limit: 0.2 atomic %).[5] A nominal pore diameter of 250 Å for the PGC particles is estimated by the manufacturer. The surface area of the carbonaceous stationary phase is *ca.* 30 m^2, based on BET adsorption measurements (120 m^2/gram) and the amount of PGC packed into the column (~0.25 g).

Table 1. *Structures of the mono- and di-valent ions employed as test solutes.*

 	Benzene Backbone					
	Acronym	Number	Concentration (μM)	X	Y	Z
	1,3-BDS	1	42	H	SO_3	SO_3
	BS	2	40	H	SO_3	H
	TS	3	49	CH_3	SO_3	H
	CBS	4	43	Cl	SO_3	H
	PTMA	5	49	H	H	$N(CH_3)_3$
	Naphthalene Backbone					
	Acronym	Number	Concentration (μM)	A	B	
	1,5-NDS	6	44	SO_3	SO_3	

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David W. Keller

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