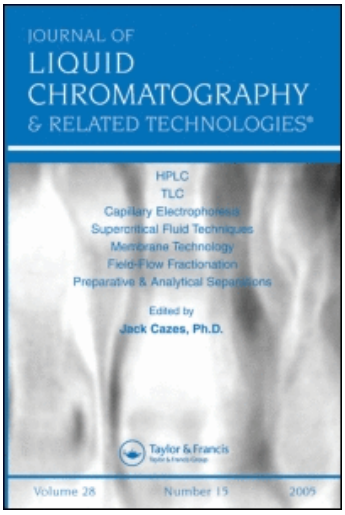

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M. S. Abdel-Latif[a]; M. D. Porter[b]
[a] Chemistry Department, The Islamic University, Gaza, via Israel [b] Chemistry Department, Iowa State University, Ames, IA

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POTENTIOSTATIC AND GALVANOSTATIC MODULATION OF LIQUID CHROMATOGRAPHY

Monzir S. Abdel-Latif,[1]* Marc D. Porter[2]

[1] Chemistry Department
The Islamic University
P. O. Box 108
Gaza, via Israel

[2] Chemistry Department
Iowa State University
Ames, IA 50011

ABSTRACT

Simplified versions of the chromatographic column in electrochemically modulated liquid chromatography were possible. A two electrodes design had a good response to changes in potential, yet excluding the need for an external reference electrode, supporting electrolyte, and porous stainless steel. The cell constants for both the two and three electrodes designs were similar. The incorporation of the reference electrode into the PVC joint of the column body resulted in fast potential equilibration times, where about a 50% decrease in the cell constant was observed using this new modification. Both the two- and the new three- electrode designs resulted in self contained, rigid, and reliable columns that can be safely dry stored; no porous stainless steel was a necessary material for the counter electrode. Galvanostatic, rather than potentiostatic, modulation of separations was successful.

Interestingly, both the two and three electrode designs resulted in identical chromatograms when the same current was used. These results suggest that the simple two electrode design with regular, rather than porous, stainless steel as the counter electrode has the same performance as that of the three electrode design, which requires an external reference electrode, external supporting electrolyte, as well as a porous stainless steel counter electrode.

INTRODUCTION

The potential of electrochemically modulated liquid chromatography (EMLC) has been demonstrated in several reports.[1-13] The control and manipulation of the nature and retention characteristics of the stationary phase by the application of potential adds a new dimension to the era of chromatographic science, and thus, deserves an additional effort in order to explore its capacity. Conventional liquid chromatographic techniques are limited by the type of stationary phase used and only manipulation of the mobile phase is allowed. However, mobile phase manipulation has a certain capacity which, in most cases, limit the use of a specific HPLC column to certain applications and some types of samples. The emergence of carbonaceous packings as stationary phases in liquid chromatography[14-18] is a significant development in the field of HPLC packing materials, especially after the introduction of the very finely clean porous graphitic carbon (PGC). This packing material has a surface area exceeding 200 m^2/g.

Among the most important advantages of PGC, in addition to its clean and high surface area, are its high mechanical strength (~ 7000 psi), excellent pH stability in the whole range from 1-14, as well as its good electrical conductivity, which makes it the packing of choice for EMLC based separations. The last two features of PGC are significant advantages over the conventionally used silica based packings. Many important applications of PGC in HPLC separations were reported, including the separation of ionic species, neutral compounds, and, interestingly, optical isomers.[19-21] Carbonaceous materials are routinely used in EMLC separations because of their good electrical conductivity. These packings act as both the stationary phase and the working electrode as well. The potential of these carbonaceous packings is usually controlled by a conventional potentiostat.

The carbon working electrode is usually a part of a three electrode (3E) electrochemical cell, in conjunction with a counter electrode and a Ag/AgCl reference electrode. The counter electrode is a porous stainless steel tubing that is part of the chromatographic column, separated from the carbonaceous stationary phase (working electrode) by a Nafion cation exchange tubing.[4-6] The

counter electrode is incorporated into an outer glass compartment containing a supporting electrolyte and the Ag/AgCl reference electrode. In this configuration, it is obvious that the porosity of the stainless steel counter electrode is essential in order to allow for electrolytic contact among the three electrodes.

Separations of different types of samples were successful using this configuration.[4-6] However, a self contained column without the need for an external electrolyte, compartments, or a reference electrode is, ultimately, sought. This anticipated column design should look very similar to conventional HPLC columns for convenience of handling, shipping, and storage.

In this report, we present results obtained excluding both the reference electrode as well as the external supporting electrolyte. Therefore, the system is treated as a two electrode cell with the carbonaceous stationary phase acting as the working electrode. In addition, a new column design in which the reference electrode was embedded into the column body is described.

Finally, separations under galvanostatic, rather than potentiostatic, conditions are evaluated which is, to the best of our knowledge, the first report that describes the utilization of constant current to effect and modulate chemical separations.

EXPERIMENTAL

Carbonaceous Stationary Phase

Three carbonaceous stationary phases were used in column construction. The first two stationary phases were nonporous glassy carbon spheres (Sigradur G, HTW, Germany). The particle diameters of the first carbon packing were in the range of 3-4 μm (type A column) while the particle diameters of the second were in the range of 6-10 μm (type B column). These two packing materials were prepared by resieving, by air classification, 0.4-12 μm Sigradur G carbon particles. The third stationary phase was a 7 μm porous graphitic carbon with an average pore size of about 80 A° (type C column), obtained from Shandon, England.

The carbonaceous materials thus obtained were used without modification or pretreatment. XPS experiments on these carbonaceous materials showed that PGC is a pure carbon with no traces of oxygen while the glassy carbon contained about 2% oxygen and 98% carbon. This was also confirmed by a Raman scattering experiments using the 488 nm laser line.

Column Packing Procedure

An appropriate amount of the desired carbonaceous spheres (~ 0.9 g) was dispersed in a 50:50 mixture of acetonitrile/dibromomethane solution. The thus obtained heterogeneous mixture was sonicated for 10 min and then the slurry was transferred to the packing compartment of a Shandon liquid chromatographic column packing unit. The dispersed spheres were then packed into the column using pure acetonitrile as a solvent for an initial period of about 30 min at about 5000 psi. The solvent was then changed to a 0.1 M lithium perchlorate in acetonitrile solution for at least 12 hrs.

Column Design and Construction

Type A and C columns had the same general design as reported previously.[5,22] The Nafion tubing which incorporated the carbon stationary phase and electrically isolated the working and counter electrodes was pretreated by boiling in ethanol for 10 min followed by boiling in 0.5 M aqueous lithium perchlorate solution for an additional 10 min. In type B column design, a fine Ag/AgCl wire was mounted inside a 1/16 in. Teflon tubing so that a very small length of the wire just exits the Teflon tubing body at the internal end of the tube.

The wire was held in place using a regular 1/16 in. stainless steel adapter and ferrule and then fixed to its exact fit in the PVC joint so that the Ag/AgCl wire and the Nafion tubing are in contact with about 50 μL of a saturated sodium chloride solution.

Instrumentation

A HP HPLC 1050 series quaternary pump and a HP 1050 series diode-array detector were the essential components of the HPLC system. Both were controlled through a HP Chemstation software using a Pentium (100MHz) processor and the output was displayed on a MicroScan 5AP/ADI monitor. A hard copy was obtained with a HP laserjet printer. All EMLC columns used in this study were packed using a liquid chromatographic column packing unit from Shandon, England.

The potential of the working electrode was controlled through a high power potentiostat from AMEL Instruments (Model 2055), Italy. A Ag/AgCl (satd NaCl) electrode was used as the reference electrode and the potential of the working electrode was adjusted with respect to this electrode. Injections were made using a Hamilton syringe via a Rheodyne injector (Model 7125).

Reagents and Chemicals

Benzenesulfonic acid, sodium salt dihydrate (BS), p-toluenesulfonic acid, sodium salt (TS), 4-hydroxybenzenesulfonic acid, sodium salt (HBS), p-chlorobenzenesulfonic acid, sodium salt (CBS), 1,5-naphthalenedisulfonic acid disodium salt (NDS), lithium perchlorate, and trifluoroacetic acid (TFA) were from Aldrich Chemical Company, Inc. Tetraethylammonium perchlorate (TEAP) was from GFS Chemicals, and dibromomethane was obtained from Eastman Kodak Company. All other chemicals and reagents were from Fisher Scientific. HPLC grade acetonitrile and deionized water from a Milli-Q water purification system were used throughout this study. All reagents were filtered through a 0.2 μm filter paper from Alltech Associates using a MFS microfiltration system.

Procedure

Unless otherwise indicated, the mobile phase was either a 0.1 M lithium perchlorate in 6% acetonitrile, solution or a 0.1 M TEAP in 2% acetonitrile, 0.1% TFA solution. The flow rate was invariably adjusted at 0.5 mL/min. Detection was carried out at 220 nm throughout this work. Enough time was allowed for column equilibration after a change in mobile phase composition, potential, or current was induced. Equilibration was assumed when a stable base line was achieved. Helium degassing of the mobile phases was utilized throughout the separation and equilibration processes.

RESULTS AND DISCUSSION

Current Column Design in EMLC

The best EMLC column design yet described in the literature is that of Ting and Porter.[22] The stationary phase, which is the working electrode as well, is separated from the porous stainless steel counter electrode by a Nafion tubing and a nonconducting PVC joint. A porous stainless steel was essential in order to allow for electrolytic contact between the carbon working electrode, porous counter electrode, and the Ag/AgCl reference electrode at the outer compartment. The external electrolyte usually contains the same salt concentration as the mobile phase. It should be realized that this setup looks very much the same as a three electrode cell in a conventional electrochemical experiment. However, changes in the porosity of the counter electrode and the potential of the reference electrode due to continuous use or storage may impose problems with regards to reproducibility.

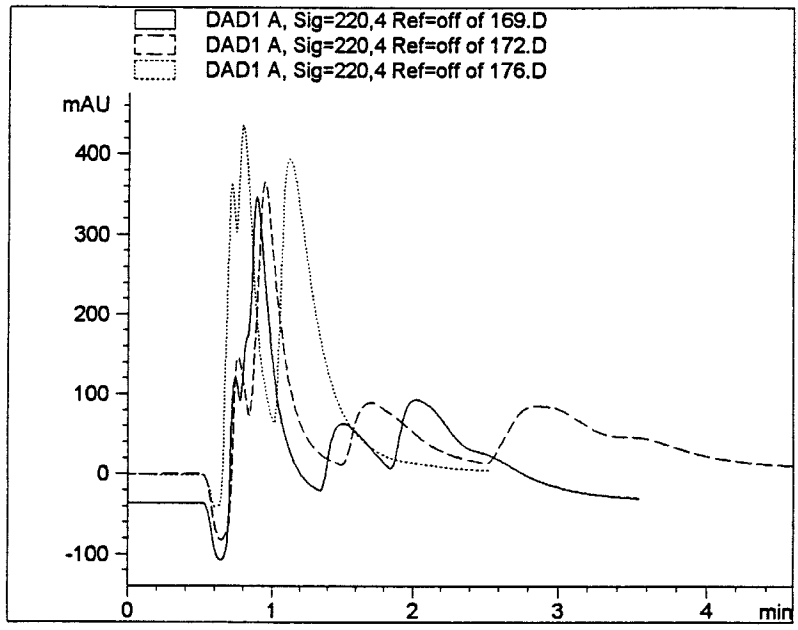

Figure 1. Overlay of chromatograms of BSF at 0.0 V (solid), +500 mV (dashed), and -750 mV (dotted). Conditions: mobile phase was a 0.1 M TEAP, 0.1% TFA, and 2% acetonitrile at a flow rate of 0.5 mL/min using type A column.

Although no such study has yet been performed to evaluate the long term performance of this design, it is realized that a self contained column, excluding the need for any external components, is a key requirement for better reproducibility and convenience of handling and storage. In this respect, we think that the column should look very much like a conventional HPLC column with the capacity for electrochemical manipulation. Therefore, we attempted to exclude the reference electrode, external supporting electrolyte, and outer compartment. The lead of the reference electrode from the potentiostat was connected to the counter electrode so that the column could be treated as a 2E electrochemical cell.

Response of the 2E Design to Changes in Potential

When potential was applied between the working electrode and the counter electrode, to which the reference electrode lead was hooked, it was observed that obvious changes in retention were recorded as the potential was varied. Figure 1

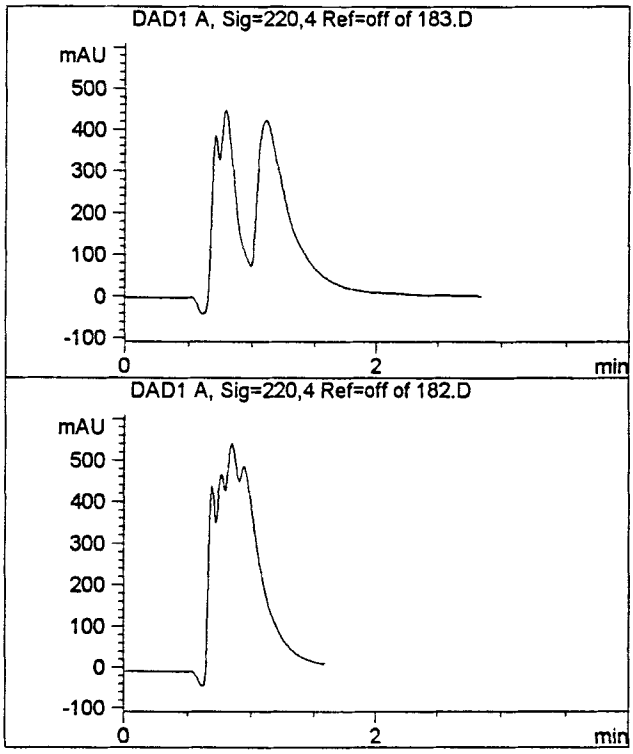

Figure 2. Chromatograms of BSF using the 2E design (upper) and the 3E design (lower). Other conditions are the same as mentioned in Figure 1.

shows an overlay of chromatograms of a mixture of benzenesulfonates (BSF) at different potentials. The dashed line represents the chromatogram of BSF at +500 mV, the solid line represents the chromatogram of BSF at 0.0 V, while the dotted line is the chromatogram of BSF at -750 mV. It is clear from the figure that significant changes in the retention behavior of the sulfonates were achieved as the potential was changed.

Sensitivity of the 2E Design to Changes in Potential

It is important, at this point, to indicate that the 2E EMLC setup showed a different sensitivity to changes in potential as compared to the 3E design. It was clear that the 2E setup encounters more positive potentials which was translated into increased retention of the BSF at any given potential, as compared to the 3E design. Figure 2 shows chromatograms of BSF using the 2E setup (upper) and

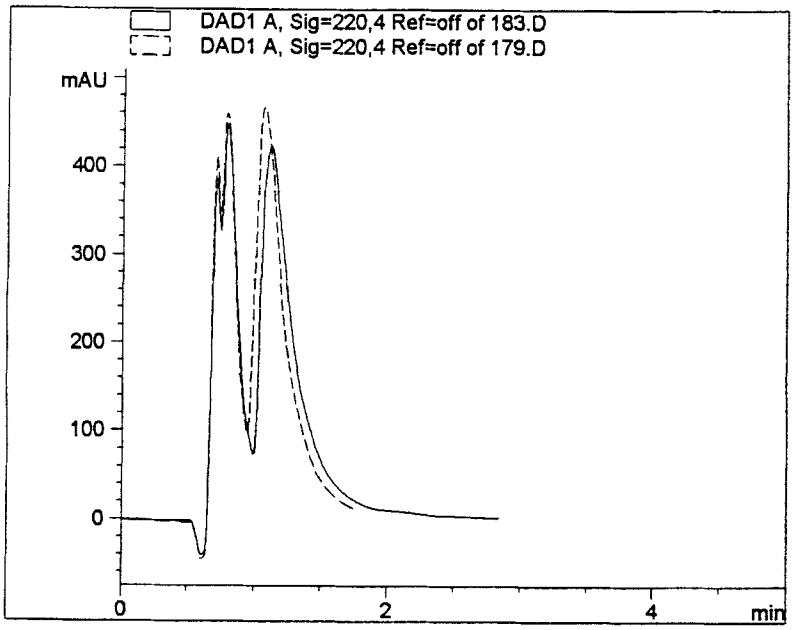

Figure 3. Overlay of chromatograms of BSF using the 2E design at -300 mV (dashed) and the 3E design at 0.0 V (solid). Other conditions are the same as mentioned in Figure 1.

the 3E design (lower) using the same conditions of mobile phase composition, flow rate, and potential. Therefore, more negative potentials would be required for the 2E system to result in the same retention characteristics of the 3E system with regards to the separation of BSF. The potential difference between the two designs was estimated to be about 300 mV (Figure 3), but it seems that this value is not constant at all potentials.

Cell Constants of the 2E and 3E Designs

The value of the cell constant is an important parameter which should be considered in electrochemical studies and is of utmost importance in EMLC experiments. Since the cell constant merely indicates how fast the working electrode can acquire the applied potential, this parameter should be well known in any EMLC experiment because it is assumed that the working electrode has the same potential as indicated by the meter of the potentiostat. It is clear from Figure 4 that both the 2E and the 3E systems have, essentially, the same cell constant. This is an interesting and important observation since no drawbacks,

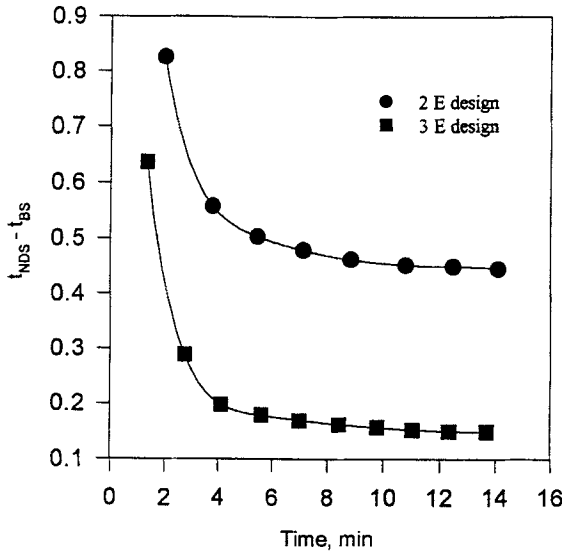

Figure 4. Relative retention of NDS versus time using the 2E design and the 3E design after the potential was changed from +500 mV to -500 mV. Other conditions are the same as mentioned in Figure 1.

in terms of response time, should be expected when the 2E design is used. Therefore, it seems advantageous to use the 2E design since a self contained column with comparable merits to the 3E system was obtained. The 2E configuration is convenient as it excludes the external compartment, supporting electrolyte, and reference electrode. Another important feature is the use of regular stainless steel tubing which adds to the rigidity, durability, and safe dry storage of the EMLC column.

New Self Contained 3E Design

Another important and very promising development in the EMLC column design involved embedding a Ag/AgCl wire into the PVC nonconducting joint so as to act as a reference electrode in a three electrode electrochemical cell. This is a very significant advantage since no external compartment or supporting electrolyte was necessary. In addition, regular, rather than porous, stainless steel was used. This resulted in a rigid column configuration, except for a problem to be mentioned later. The Ag/AgCl wire was fitted into a 1/16 in. Teflon tubing and a regular stainless steel ferrule held the wire in place which was then fitted into the PVC joint by a 1/16 in. stainless steel adapter. A very small hole in the

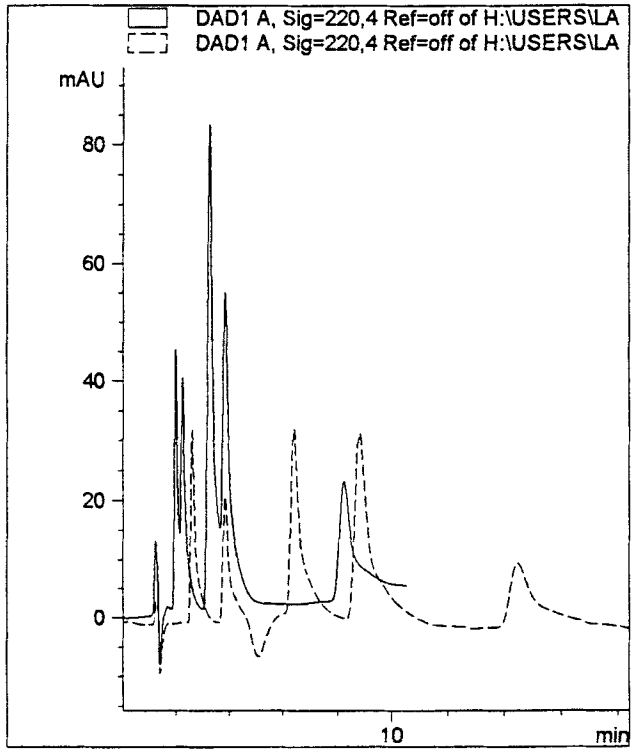

Figure 5. Overlay chromatograms of BSF at open circuit (dashed) and at -1.2 mA using the 2E configuration. The mobile phase was an aqueous 0.1 M lithium perchlorate / 6% acetonitrile solution. Type C column was used at a flow rate of 0.5 mL/min.

PVC joint and a drop of saturated sodium chloride solution allowed for the electrolytic contact among the reference and working electrodes. Interestingly, this new version of column design showed excellent performance where about 50% decrease in cell constant was observed as compared to the previous 3E design. Therefore, the new EMLC column design has very fast potential equilibration times in addition to excluding all external components, as well as, the necessity for porous stainless steel counter electrode. A self contained, rigid, and very convenient system was achieved. However, occasional recharge of the saturated sodium chloride solution was necessary. We attribute this to evaporation due to loose fitting of the reference electrode body, a problem which could be overcome by proper adjustment of the Teflon/Ag/AgCl ferrule fitting and that of the adapter/ PVC connection.

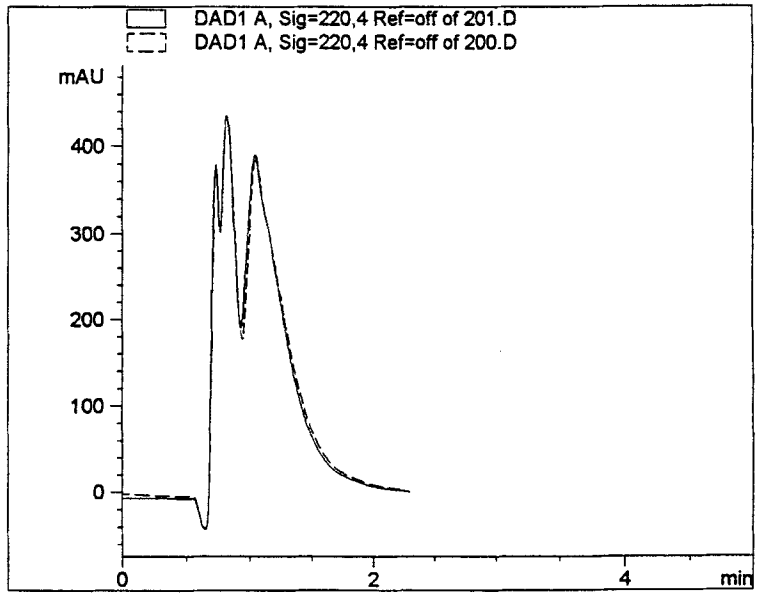

Figure 6. Overlay of chromatograms of BSF using the 2E design (solid) and the 3E design (dashed) both at -0.1 mA. Other conditions are the same as mentioned in Figure 1.

Galvanostatic Control of Separations

Since the beginning of its emergence, EMLC has been concerned with the procedure through which the potential of the working electrode is controlled by the application of a preset potential or potential ramp. We have studied the possibility of galvanostatically controlling a separation in both 2E and 3E EMLC column designs. This approach was anticipated to expand the scope of EMLC and provide a further dimension towards understanding the mechanism of separation under these conditions.

Figure 5 shows an overlay of chromatograms for BSF at constant current (solid line) and at open circuit (dashed line) using a 2E design. It is obvious from the figure that passage of current between the working and counter electrodes resulted in a significant change in the retention characteristics of BSF. Therefore, it was decided to conduct some further detailed experiments on this approach so as to evaluate its capacity and merits.

Galvanostatic Separations using 2E and 3E Designs

When separations of BSF were performed under galvanostatic conditions with 2E and 3E column designs, a rather astonishing and very interesting behavior was observed. When the current was fixed at a specific value, chromatograms of BSF using either the 2E or 3E design were identical. This suggests that the passage of current may be the driving force for the change in the retention characteristics of solutes in EMLC experiments. This also suggests that the self contained and rigid 2E design would be the right choice when operating under galvanostatic conditions because of its simple design. Figure 6 shows an overlay of two chromatograms at constant current using the 2E (solid line) and the 3E (dashed line) designs. It is interesting to indicate that these two chromatograms were obtained at very different output potentials. Therefore, the use of galvanostatic separations seems to offer very important advantages in terms of the possibility of using simplified column designs since same results could be obtained with either the 2E or 3E designs.

This development should also result in a high performance, rigid, and self contained EMLC column with no external supporting electrolyte, reference electrode, or porous stainless steel counter electrode. It would be very interesting to study the long term reproducibility of the 2E and 3E column designs under both potentiostatic and galvanostatic operating conditions. Another relevant improvement would be to find some suitable combinations of current and solvents which can routinely be used for column clean up since carbon packings are easily contaminated and are difficult to clean especially after prolonged use.

Effect of Electrolytes on Retention at Constant Current

We have previously shown that retention behavior of BSF, under potentiostatic conditions and open circuit potentials, was a function of electrolyte type.[23] It was also observed that an electrolyte type plays an important role in separations under galvanostatic conditions, in the same manner as it does under constant potential EMLC experiments. Figure 7 shows such an effect on the retention behavior of BSF using a 3E design at constant current. The solid line chromatogram was obtained using an aqueous mobile phase that is 0.1 M KCl, 0.1% TFA, and 7% acetonitrile. The dashed line chromatogram was obtained using an aqueous mobile phase composition of 0.1 M TEAP, 0.1% TFA, and 2% acetonitrile. A large decrease in the retention of BSF took place when the electrolyte was changed from KCl to TEAP, even at much lower acetonitrile concentration. Therefore, it is always an advantage to select the right mobile phase when planning EMLC separations under potentiostatic or galvanostatic conditions.

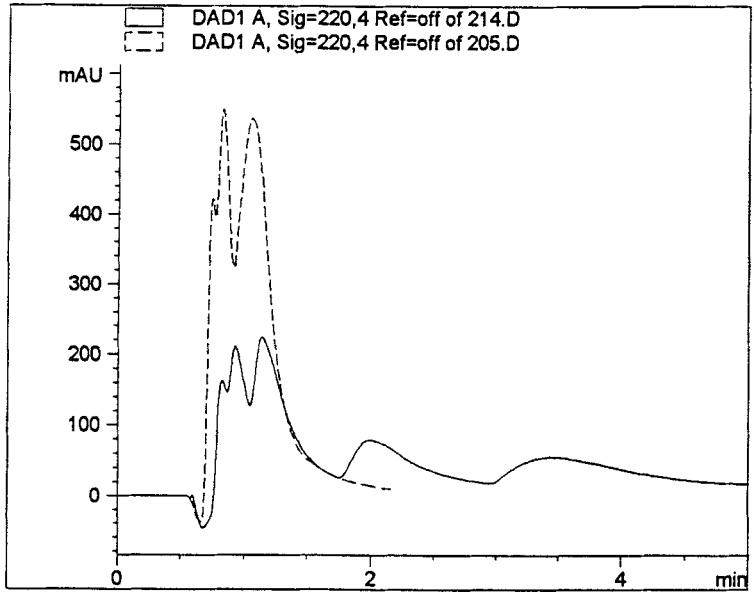

Figure 7. Electrolyte effects on the retention characteristics of BSF using the 3E design (type A column). The solid line chromatogram was obtained using an aqueous mobile phase composition of 0.1 M KCl, 0.1% TFA, and 7% acetonitrile. The dashed line chromatogram was obtained with an aqueous mobile phase containing 0.1 M TEAP, 0.1% TFA, and 2% acetonitrile. The flow rate was adjusted at 0.5 mL/min in both experiments.

Retention of BSF as a Function of Current Density

The retention of the different BSF is differently affected by changes in current density. The same trend as observed under constant potential was also observed using constant current EMLC separations. Chromatograms of BSF obtained at open circuit and at constant current experiments are shown in Figure 8. The top chromatogram was obtained at open circuit. The chromatogram in the middle represents the separation of BSF at a constant current of -0.5 mA, while the chromatogram at the bottom of the figure was obtained at a constant applied current of -1.2 mA. It is clear from the comparison of these chromatograms that significant changes in the capacity factors of the different compounds takes place as a result of changes in the applied current density. Also, it is worth mentioning that the peak representing NDS traveled in a higher rate as current density was increased in the negative direction, and even elution before TS was observed as shown in the figure (bottom chromatogram). The other significant observation concerns the HBS peak which did not disappear as

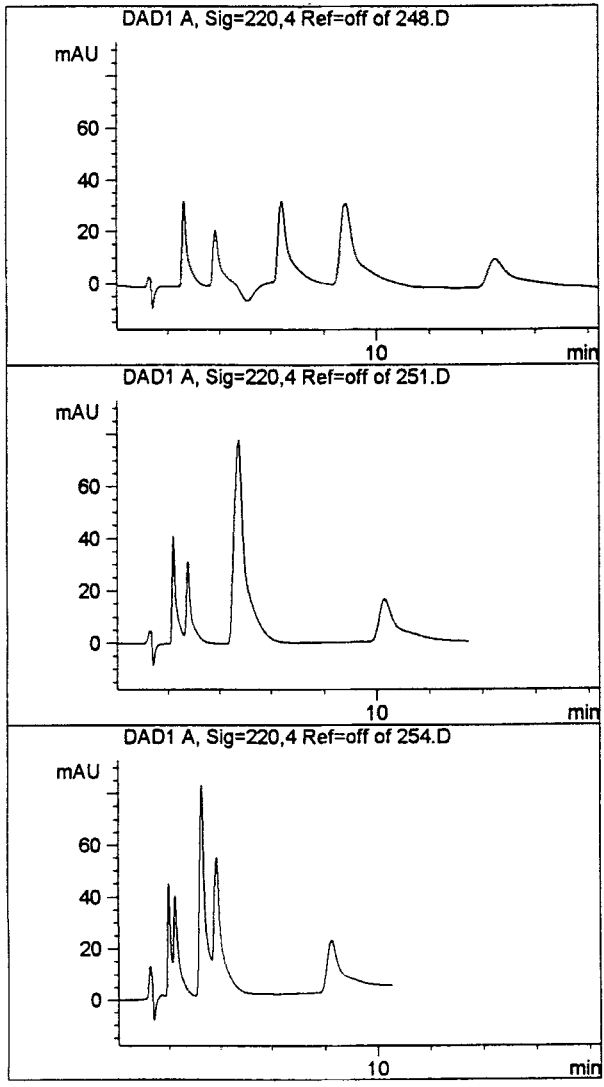

Figure 8. Retention of BSF as a function of current density. Chromatograms were obtained at open circuit (top), -0.5 mA (middle), and -1.2 mA (bottom). Other conditions are the same as mentioned in Figure 5.

the current density was increased in the negative direction. A behavior that is completely different from that observed in EMLC experiments under constant potential where the HBS peak disappears, is due to oxidation, and coelutes with BS. A plot of log K` versus current density was linear in the current range from 0.5-1.2 mA in the negative direction. It is also clear from the figure that NDS retention has the highest sensitivity to changes in current density, as compared to the other sulfonates tested. The slopes of the different straight lines can be qualitatively related to the density of the available overall negative charge on each compound. Therefore, the sensitivity of BSF components to manipulation by the application of current is in the order NDS>HBS>BS>CBS which was experimentally observed.

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