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Capillary Electrochromatography with Fused-Silica Capillaries Packed with Copolymeric Reversed-Phase Adsorbent and Ion Exchangers

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Macroporous poly(styrene−divinylbenzene) (PSDVB), PRP-1, a reversed-phase adsorbent, and PSDVB-based strong acid cation exchangers and strong base and weak base anion exchangers were evaluated as stationary phases for capillary electrochromatography (CEC). Electroosmotic flow (EOF) for adsorbent and exchanger packed fused-silica capillaries for acetone as the marker increases with increasing ion exchange capacity, buffer organic solvent concentration, and applied voltage, is nearly independent of pH, and decreases with increased buffer ionic strength. For anion exchangers, EOF is reversed. Thiourea, acetone, acrylamide, nitromethane, propanal, and acetic acid were evaluated as EOF markers and undergo weak interaction with the PSDVB-based stationary phases. EOF in a basic buffer is greater than or equal to silica-based C-18 and cation exchanger packed capillaries. For an acidic buffer, EOF for a PRP-1 capillary is almost twice the C-18 packed capillary. As analyte hydrophobicity increases, retention and migration time increases for the PSDVB-based stationary phases. As exchange capacity increases, availability of the polymeric matrix for analyte partitioning decreases, causing analyte migration time to decrease. Increasing buffer organic solvent concentration decreases analyte retention. The PSDVB-based stationary phases provide good resolving power and reproducibility and are applicable to the CEC separation of neutral, weakly acidic, and basic analytes. Efficiency, however, is less than obtained with silica-based stationary phases. Because of stability in a strong acid buffer, the CEC separation of weak acids, where dissociation is suppressed, and weak bases as cations is possible. Separations of short-chain alkyl aldehydes, methyl ketones, aromatic hydrocarbons, substituted benzene derivatives, and short-chain carboxylic acids are described.

Capillary electrochromatography (CEC) is a hybrid technique that combines the partitioning effects of high-performance liquid chromatography (HPLC) with the electrophoretic and electroosmotic electrically driven forces of capillary electrophoresis (CE) in a fused-silica capillary packed with a stationary phase.[1−4] Three types of packed capillaries are currently used in CEC. The most common type is a fused-silica capillary packed with small, uniform particles of a solid stationary phase, typically a silica-based C-18 stationary phase.[1−14] A second type is a monolithic or continuous bed capillary where the stationary phase is synthetically prepared as a solid porous form in the capillary.[15−18] An advantage of this type of capillary for CEC, in addition to the potential to employ novel stationary phases such as monolithic silica, is that inlet and outlet frits are no longer required. The third type is a fused-silica capillary wall coated with a neutral group, ionic group, or a copolymer via chemical bonding as a thin film.[3,19] This strategy has also been widely used in CE to reduce the effect of the silanol sites on analyte wall adsorption, to alter EOF, and/or to create unique centers for analyte interaction. For chemical bonded modified surfaces, C-18,[19,20] C-8,[21] and neutral and ionic polymer coatings[19,22,23] have been bonded to the fused-silica capillary wall via the silanols and used to separate polyaromatic and other neutral analytes by CEC. Negatively charged bonded sulfonic acid groups[24−26] produce an electroosmotic flow (EOF) that is nearly

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constant over the pH range of 2−10 (in contrast to the bare fused-silica capillary whose EOF rises sharply in the vicinity of the silanol pK_a). In addition, the EOF is higher in an acid buffer, which makes this capillary particularly useful for separating weak bases as cations.[27,28] In contrast, chemically bonded positively charged quaternary ammonium groups will reverse EOF.[23,24,27−31] β- and γ-cyclodextrin groups have been chemically bonded to silica wall and used for chiral-CEC separations.[32] Other novel bonded-type capillaries include chemically bonded liquid crystals[33] and sol−gel modifications.[34]

Typical CEC stationary-phase particles are 3- and 5-μm silica-based C-18 particles[1−14] which are packed into 50-μm-i.d., centimeter-length fused-silica capillaries. Plate numbers of $>10^5$ are usually obtained.[2−4] Plate numbers as high as 40×10^6 plates/m have been reported[16] for 3-μm C-18 and a CO_2 supercritical fluid packing procedure, but its lifetime at this efficiency was short. Other stationary phases have been employed in CEC. For example, alkyl alumina-based particles for separations in an alkaline buffer,[35] ethylene chlorotrifluoroethylene particles,[36] and stationary-phase materials trapped in a silicate network[37] have been used. Chiral bonded-phase particles,[38] cyclodextrin-modified particles,[39−41] and aminopropyl silica gel particles coated with helically chiral poly-(diphenyl-2-pyridylmethyl) methacrylate[42] were used for chiral separations.

Fused-silica capillaries packed with cation or anion exchange stationary phases have been used in CEC studies.[13,14,43−59] In some cases, silica-based C-18 and ion exchangers are mixed[51] prior to packing the capillary while in others silica particles are chemically modified to contain both alkyl and sulfonated[49,50,52] or anion exchange groups.[55,58,59] Thus, a mixed-mode type of migration mechanism of electrophoretic, electrostatic, and partitioning/adsorption is possible. General observations with silica-based ion exchangers in CEC are the following: (1) EOF increases with ion exchange capacity. (2) EOF tends to decrease with buffer ionic strength and increase with an increase in acetonitrile concentration in aqueous acetonitrile mixtures particularly for the stationary phases capable of a mixed-mode type interaction. (3) EOF is reversed for the strong base ion exchangers. (4) EOF is nearly independent of pH, peak efficiencies are favorable particularly for the cation exchanger, and properties such as the effects of applied voltage and current generated are similar to what is experienced with C-18 packed capillaries. (5) A mixed-mode separation mechanism is possible depending on the silica-based stationary phase and its modifications.

CEC separations were reported for alkybenzene derivatives,[49] basic pharmaceuticals,[11−13,54] carboxylic acids, aniline, and pyridine derivatives,[50,51,54] nucleosides,[50] peptides and proteins,[52,53] and alkaline metals, transition metals, and rare earths[47] with capillaries packed with silica-based cation exchangers. Inorganic anions,[43,46,56] peptides and proteins,[55,59] benzoic acid derivatives,[57] and herbicides[58] were separated with silica-based anion exchanger packed capillaries. A silica-based cation exchanger charged in the cetyltrimethylammonium form was used to separate acidic, basic, and neutral analytes with a buffer also containing the $R_4N^+Br^-$ salt as an additive.[46]

Choudhary and Horváth[10] examined a highly porous poly-(styrene−divinylbenzene) (PSDVB) copolymeric reversed-phase adsorbent as a CEC packing material. They found EOF at pH 8.0 and high field strength to be about one-third of the EOF obtained for an open tube capillary and about half of the EOF for a C-18 packed capillary. When a sulfonated copolymer was used, EOF increased. No detailed studies were reported on the potential applications of polymeric reversed-phase adsorbents or copolymeric-based ion exchangers in CEC, although the CEC separation of two tetrapeptides at high column efficiency was reported using an acetonitrile/aqueous 25 mM phosphate, pH 3.5 (2:3 v/v) buffer. A PRP-1 fused-silica packed capillary was successfully used for the CEC separation and electrospray mass spectrometric detection of aromatic glucuronides.[60]

The PSDVB stationary phase has several advantages compared to a silica-based C-18 stationary phase in LC separations.[61] For example, PSDVB is highly porous, is stable throughout the entire pH range and, in mixed solvents, is an adsorbent that exhibits high-capacity factors for a wide range of basic, acidic, and neutral analytes, is free of residual silanol sites, and provides linear isotherms. It has high analyte loading capacity and a surface that can be chemically modified. Its major disadvantage is a slower

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mass transfer, which leads to broader analyte bands and lower column efficiency.

In this report, CEC studies with fused-silica capillaries packed with a macroporous PSDVB copolymeric reversed-phase adsorbent, PRP-1, and cation and anion exchangers derived from this copolymeric matrix are described. The presence of strong acid, SO_3H^+, or strong base, $R_4N^+X^-$, ionogenic exchange sites on the PSDVB copolymer matrix not only provides sites for analyte interaction and affects EOF but also influences the availability of the PSDVB matrix for reversed-phase partitioning. This in turn will influence partitioning and migration time of neutral and charged analytes that also have hydrophobic centers. Properties affecting EOF are established and a survey of applications of a fused-silica capillary packed with adsorbent or ion exchanger stationary phase is described.

EXPERIMENTAL SECTION

Instrumentation and Materials. The CEC instrumentation used was an in-house-assembled modular unit composed of a Spellman high-voltage dc power supply model UHR, 0−30 kV (Spellman High Voltage Electronics Corp.), a Spectra Physics 100 UV−visible variable-wavelength detector equipped with an on-column capillary accessory (model 9550-0155), and a packed fused-silica capillary. All packed capillaries were made from 75 μm i.d. × 365 μm o.d. polyimide-coated fused-silica capillary (Polymicro Technologies). Platinum electrodes connect the power supply to the inlet and outlet buffer reservoirs at the capillary ends. To prevent electrical shock, the packed capillary inlet end was enclosed in a Plexiglas box with a safety interlock system during operation. Data were collected and processed with a Spectra Physics M-4270 integrator controlled by Spectra Physics Autolab Software. All CEC measurements were done in the absence of an applied pressure.

All analytes used as received were analytical reagent grade when possible and were obtained from Aldrich Chemical Co., Eastman Organic Co., Fisher Scientific, Mallinckrodt Chemical Works, and Sigma. Acetonitrile, methanol, and ethanol were HPLC grade and obtained from Fisher, Em Science, and Pharmco Products, respectively. In-house distilled water was passed through a Milli-Q-Plus water treatment unit equipped with a final 0.2-μm filter and was used to prepare all samples and buffer solutions.

All stationary phases used to pack the fused-silica capillaries were obtained in bulk form from Hamilton Co. They are macroporous and have a PSDVB coploymeric matrix, and their key physical properties are listed in Table 1.

Column Preparation. Fused-silica capillary was cut to a ∼50-cm length, washed with acetonitrile and aqueous 0.5 M NaOH solution, and dried by flushing with air prior to frit formation. The initial frit was formed using a modified procedure[62] and serves as the outlet frit in the packing procedure and the inlet when the packed capillary is used in a CEC application. A small amount of 5-μm silica gel particles (Amicon Corp.) wetted with ∼1:1 H_2O/Na_2SiO_3 (v/v) to form a paste was tapped into the capillary end to form a zone of ∼0.5 mm in length. The silica zone was gently heated and fused into a frit using a temperature-controlled device connected to a thermal wire stripper (Kinetics Teledyne Co.). A slurry of the stationary phase (∼1:10, w/v) in 1:1 degassed ethanol/water (v/v) was ultrsonicated for ∼10 min to break any agglomerates, and the slurry was then transferred to an empty 10 cm × 2.1 mm i.d. stainless steel HPLC column which served as the slurry packing reservoir. The capillary protruded ∼5 cm into the slurry solution in the packing reservoir and was connected by PEEK tubing and fittings to a Beckman model 110A HPLC pump. The slurry solution and degassed 1:1 ethanol/H_2O were pumped into the capillary at a rate of 0.1 mL/min with back pressure that approached 6000 psi. When a packed bed length of 20 cm was obtained, the pressure was slowly released. A slurry of silica gel particles in 1:1 degassed ethanol/H_2O was than placed in the packing reservoir, and a small amount of the slurry was pumped into the capillary to form a silica gel bed of about 2−3 mm at the top of the packed bed. The solvent in the capillary was replaced by degassed water, and this was slowly pumped through the packed capillary at ∼3000 psi while forming the second frit and the optical window. The second frit (serves as the outlet frit in the CEC application) was formed as described previously out of the 2−3-mm silica bed, being very careful to avoid disturbing the packed stationary phase. After formation of the frit, an optical window was prepared on the capillary by carefully burning away ∼5 mm of the polyimide coating as close as possible to the CEC outlet frit. A microscope was used to examine the capillary during the entire procedure and other stages of CEC studies with the capillary. The excess length of open tube fused silica was cut off to yield a packed capillary of 20 cm effective or packed length. The total capillary length was 30 cm for the reversed phase and cation exchanger and 27 cm for the anion exchanger packed capillaries. Each capillary was conditioned with the appropriate buffer solution preceding each CEC study.

Procedures. Buffers used in this study were prepared in degassed water or organic solvent-buffered water mixtures (v/v). Buffer solutions included phosphate (5−10 mM), tris-(hydroxyamino)methane (TRIS) and its hydrochloride salt (10−30 mM), and H_2SO_4 (5−10 mM). Buffer concentrations were kept low enough so that current passed (at 10 kV) was usually about 1−2 μA (always <10 μA) but high enough to have suitable buffer capacity. The higher buffer concentrations were often used with the lower capacity exchanger and PRP-1 packed capillaries.

Table 1. Physical Properties of the Stationary Phases

Reversed Stationary Phase Adsorbent
PRP-1, PSDVB copolymeric adsorbent, 7 μm
Strong Acid Cation Exchanger
PRP-X300, $-SO_3^-$ exchange site, 7 μm, 0.17 mequiv/g of exchange capacity
PRP-X400, $-SO_3^-$ exchange site, 5 μm, 5.0 mequiv/g of exchange capacity
Strong Base Anion Exchanger
PRP-X100, $-R_4N^+$ exchange site, 5 μm, 0.19 mequiv/g of exchange capacity
RCX-10, $-R_4N^+$ exchange site, 7 μm, 0.35 mequiv/g of exchange capacity
RCX-30, $-R_4N^+$ exchange site, 7 μm, 1.0 mequiv/g of exchange capacity
Weak Base Anion Exchanger
PRP-X700, aminopropyl exchange site, 7 μm, 1.4 mequiv/g of exchange capacity

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Degassing of all solutions was >20 min by stirring and aspiration. Buffer solution in the outlet and inlet vials were frequently replaced depending on the number of runs. Stock solutions of 1−10 mg/mL analytes were prepared in aqueous buffer/acetonitrile solutions. Known aliquots were taken and diluted with buffer to yield an analyte solution of about 0.1−1 mg/mL.

For each study, the packed capillary was first positioned in the Plexiglas enclosure with the capillary ends in buffer inlet and outlet vials with the detection window placed appropriately in the detector. For reversed-phase or cation exchanger packed capillaries, the cathode was at the detector end of the capillary and the anode was at the inlet. For anion exchanger packed capillaries, the detector end was the anode due to reversed EOF. Detection was usually done at 214 or 254 nm. The capillary was then conditioned at 10 kV with the given buffer and allowed to set containing the buffer for ∼1 h prior to initiating the study. Packed capillary performance was verified initially and repeatedly during the study using acetone as the analyte marker. Acetone was also used as the EOF marker except where noted. Sample injection was by electrokinetic injection, usually for 5−10 s at 1 kV. Sample sizes typically injected were about 1−50 pmol depending on the chromophoric properties of the analyte and the experimental conditions. All measurements were done at ambient temperature or 23 °C and in the absence of applied pressure. Capillary lifetime, which depended on the number of changes in buffer conditions and bubble formation that randomly occurred at the inlet frit, varied from several days to several months. Results reported here are averages typically for more than three independent runs and reproducibility for the acetone marker was typically ±2.0%. When not in use, the packed capillaries were stored containing 4:1 acetonitrile/aqueous 20 mM TRIS−TRIS-HCl, pH 7.0 (v/v) with the capillary end also inserted in the buffer solution. Analyte peak position in mixtures was verified by comparison to individual standards and by analyte spiking techniques. Peak efficiency for the packed capillaries for the acetone marker typically were ≥5 × 10^4 plates/m, depending on the stationary phase and conditions.

RESULTS AND DISCUSSION

EOF, Analyte Marker Structure, and Applied Voltage. Macroporous copolymeric PSDVB stationary phases in LC provide surfaces that exhibit strong adsorptive properties toward analytes that cover a wide range of hydrophobicity.[61] When ion exchange groups are chemically bonded, adsorptive properties of the PSDVB matrix decrease as the ion exchange capacity increases. These groups also provide sites for electrostatic interactions. Thus, the PSDVB low-capacity ion exchangers are capable of exhibiting dual-type retention mechanisms of ion exchange and partitioning/adsorption via the exchanger PSDVB matrix. As stationary phases in CEC applications, the ion exchange groups should also influence EOF generated in the packed capillary.[10,13,34−59]

Previous studies with silica-based packed capillaries indicate that EOF in the packed capillary is about 40−60% lower than the EOF for an open tube fused-silica capillary.[1,7] Double layers around the particle, and to a lesser extent at the capillary wall, are suggested to be the factors that contribute to the EOF.[3−6,10,11] Studies, which are reviewed elsewhere,[63] however, have also indicated that the packed capillary exit frit also contributes to the EOF. Initial studies to establish EOF for the PSDVB based packed capillaries (see Table 1) indicated that simple, uncharged, chromophoric analytes typically used as EOF markers in open tube fused-silica CE and C-18 CEC differed in migration times, suggesting that these analytes are interacting, although weakly, with the PSDVB matrix. Table 2 lists the migration times for six different EOF analyte markers for an acetonitrile/aqueous 10−30 mM TRIS−TRIS-HCl, pH 7.0 (4:1, v/v) buffer solution and 10 kV. The most polar compound, thiourea, migrates the fastest for the PRP-1 and PRP-X300 columns but for the other columns acetone, as the marker, is the fastest. The EOF values that were calculated for the six analyte markers are also included in Table 2. For the high-capacity cation exchanger, PRP-X400, EOF is almost 70% higher compared to the absence of the exchange site, PRP-1, while for the anion exchanger of high capacity, PRP-X700, the EOF is reversed to the greatest extent. Thus, increasing the number of exchange groups in the polymer increases the EOF for the cation exchanger and increases EOF (expressed as a reversed EOF) for the anion exchanger. When comparing cation and anion exchangers of similar low exchange capacities, for example, PRP-X300 and PRP-X100, respectively, EOF for the former is over twice the EOF for the anion exchanger packed capillary. However, as high exchange capacity is approached, the difference in EOF for the two types of exchangers disappears.

Table 2. Analyte Marker Migration Times and Their EOF Values[a]

	migration time, min	
analyte	PRP-1	PRP-X300
thiourea	5.25	4.50
acrylamide	5.30	4.50
acetone	6.00	4.74
nitromethane	6.10	4.90
propanaaldehyde		5.72

	EOF ($\times 10^{-4}$ cm^2 V^{-1} s^{-1})[b]
reversed-phase adsorbent	
PRP-1	1.7
cation exchanger	
PRP-X300; PRP-X400	2.3; 2.8
anion exchanger[c]	
PRP-X100; RCX-10; RCX-30; PRP-X700	1.1; 1.3; 2.7; 2.9

[a] A 4:1 acetonitrile/aqueous 10 or 30 mM TRIS−TRIS-Cl, pH 7.0 (v/v) buffer solution. [b] Acetone as the analyte marker. [c] Reversed EOF.

The structure of the simple analyte marker also had an effect on migration time and therefore, the calculated EOF. This is illustrated in Figure 1, electrochromatograms for a mixture of three neutral analytes; two (thiourea and acetone) are typically employed as EOF markers. A 4:1 acetonitrile/aqueous 20 mM TRIS−TRIS-HCl, pH 7.0 (v/v) buffer at an applied 20 kV was used. The migration order for PRP-1 is thiourea, the most polar analyte, followed by acetone, and finally benzene, the most hydrophobic analyte. As expected, benzene analyte has a significant partitioning between the buffer and reversed stationary-phase adsorbent as it is electrically driven through the capillary. More surprising is that the simple neutral analytes, thiourea and acetone, also partition

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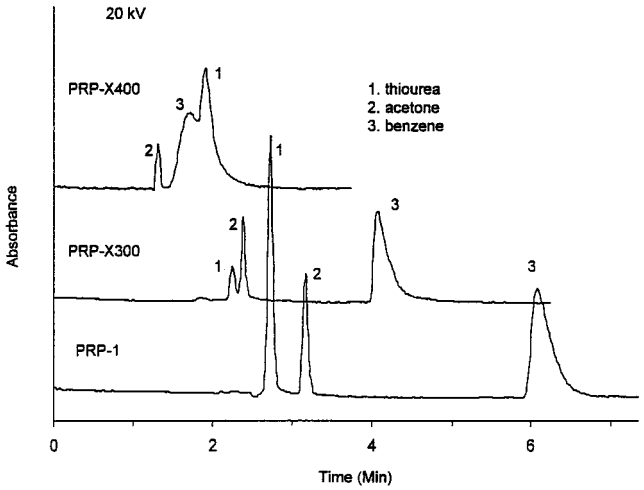

Figure 1. CEC separation of frequently used EOF markers on PSDVB adsorbent and low- and high-capacity cation exchangers. A 75 μm i.d. $\times$ 20.0 cm effective length packed fused-silica capillary and a 4:1 acetonitrile/aqueous 10−30 mM TRIS−TRIS-HCl, pH 7.0 (v/v) buffer at 20 kV.

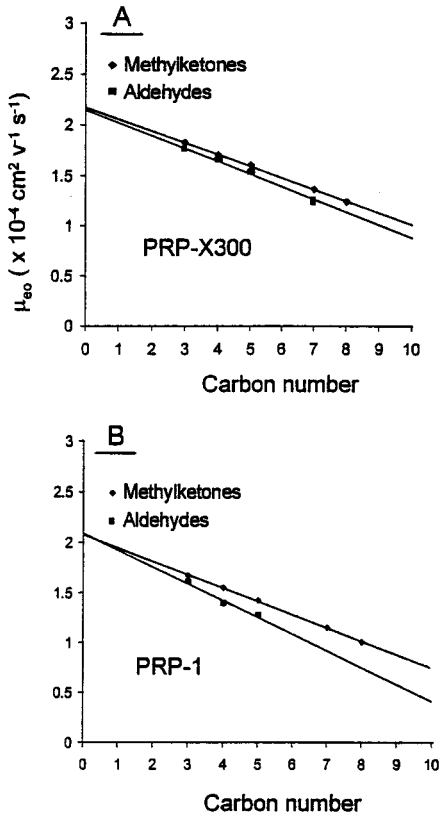

Figure 2. EOF as a function of analyte carbon number for short linear alkyl chain aldehydes and methyl ketones on a PSDVB adsorbent and a low-capacity cation exchanger packed capillary. Conditions are the same as Figure 1 except for an applied voltage of 10 kV.

to some extent and enough so that the two are actually baseline resolved. For a low cation exchange capacity, see PRP-X300 in Figure 1, migration order stays the same but migration time is reduced for all three analytes. While EOF slightly increases for the PRP-X300 versus the PRP-1, reduced migration time is due more to the effect of the charged cation exchange sites on the PSDVB surface. They reduce, but do not eliminate, the availability of the copolymeric matrix for reversed-phase activity. For a large cation exchange capacity, which significantly reduces the availability of the PSDVB matrix, migration time decreases and migration order of the analytes is changed. Hydrophobic benzene now moves quickly through the packed capillary while the most polar analyte, thiourea, moves the slowest. This order is now consistent with PRP-X400 acting as a normal phase. If the applied voltage is decreased from 20 to 10 kV, the trends are the same except that all migration times are increased due to the decreased EOF at the lower applied voltage.

When the anion exchanger packed capillaries were tested with the three analytes and the same buffer solution and applied voltage of −10 kV (EOF is reversed and thus the applied voltage polarity is reversed), migration order was found to be acetone first, followed by thiourea, and then benzene. This was observed for all four anion exchanger packed capillaries; in addition, the three analytes are baseline resolved in all cases. As anion exchange capacity increases, analyte migration time decreases, again indicating the reduced availability of the polymer matrix to participate in reversed-phase partitioning. The biggest effect was for the very high, strong and weak base anion exchange capacity stationary phases, RCX-30 and PRP-X700, respectively, where the migration time for benzene was ∼7 min versus 14 and 18 min for the lower anion exchange capacity RCX-10 and PRP-X100 packed capillaries. At the high exchange capacity, the highly charged surface (even the weak base anion exchanger is in the cation form at the pH used) minimizes the availability of the PSDVB matrix for partition effects.

A second approach to establish EOF was to calculate EOF values from migration times for an homologous series of simple analytes for a given buffer condition and compare these data to analyte carbon number. This procedure is commonly used in LC/GC to obtain retention indexes. Panels A and B of Figure 2 correlate analyte EOF with analyte carbon number for a series of short-chain simple aldehydes and methyl ketones for PRP-X300 and PRP-1 packed capillaries, respectively. As carbon number increases, migration time increases, indicating an increase in partitioning of the neutral aldehyde and ketone analytes between the stationary phase and the buffer solution as the analytes are electrically driven through the packed capillary. Extrapolation to zero carbon number gives an EOF for the aldehydes and ketones of 2.15×10^{-4} and 2.18×10^{-4} cm^2 V^{-1} s^{-1}, respectively, for the PRP-X300 capillary. For PRP-1, the extrapolated EOF is 2.10×10^{-4} and 2.08×10^{-4} cm^2 V^{-1} s^{-1} for the aldehydes and ketones, respectively. When similar studies were done with short linear alkyl chain carboxylic acids from C-2 to C-10, extrapolation to zero carbon yielded an intercept of EOF of 2.15×10^{-4} cm^2 V^{-1} s^{-1} for the PRP-X300 packed capillary. For the carboxylic acid analytes, the electrolyte solution was 4:1 acetonitrile/aqueous 10 mM H_2SO_4 (v/v) at 10 kV. The strong acid solution ensures that the carboxylic acid analytes are undissociated. As outlined in the next section, EOF is only slightly lower even at this strongly acidic condition. It can be concluded that simple analytes as markers may not truly define the EOF for the polymer and exchanger packed capillaries. Even the simplest neutral analytes may undergo some degree of partitioning between the stationary phase and the buffer solution as the analytes are electrically driven through the

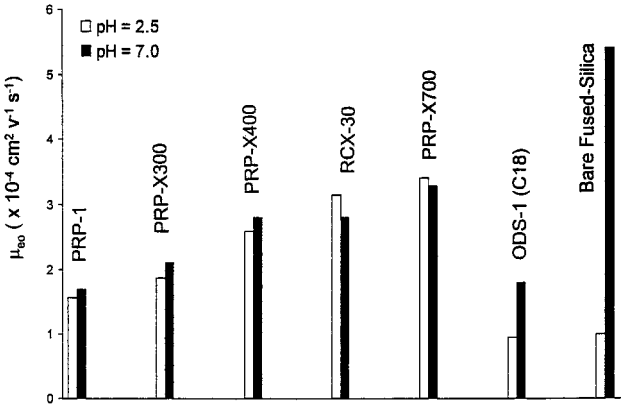

Figure 3. Effect of buffer pH on EOF for the PSDVB-based stationary phases, silica-based C-18, and open tube fused-silica capillary. Conditions for the PSDVB-based stationary phases are the same as Figure 1 except pH 2.5 and 7.0 and 10 kV and acetone as the marker. The data for C-18 and open tube fused-silica capillaries are from ref 14 and are for 7:3 acetonitrile/aqueous NaH_2PO_4−Na_2HPO_4 (v/v) buffers.

packed capillary. Whether this extrapolation procedure yields a correct value for EOF remains to be established. Because acetone usually yielded the fastest migration time, acetone was usually used as the EOF marker in subsequent studies.

Increasing the applied voltage increases the EOF for PRP-1 and the cation exchanger packed capillaries. Using acetone as the marker and a buffer that was 4:1 acetonitrile/aqueous 20 mM TRIS−TRIS-HCl, pH 7.0 (v/v), the slope for a plot of EOF versus applied voltage was 4.2×10^{-9}, 4.0×10^{-9}, and 9.0×10^{-9} cm^2 V^{-2} s^{-1} for PRP-1, PRP-X300, and PRP-X400, respectively, over the applied voltage range of 5−25 kV (excessive capillary heating was not detected over this voltage change). The near-linear increase in EOF with increased applied voltage was also observed for C-18[10] and silica-based cation exchanger[45,48,49] packed capillaries. Thus, the higher cation exchange capacity, PRP-X400, packed capillary has the largest increase in EOF with increased applied voltage; however, the rate of change in EOF with applied voltage starts to decrease as 25 kV is approached, which may be caused by the high exchange capacity. For the anion exchangers, the EOF, which is in the negative direction, becomes more positive at a much slower rate compared to the low-capacity cation exchangers when the applied voltage was varied from 5 to 25 kV.

pH. For an open tube fused-silica capillary, EOF is low in acidic solution and high in basic solution with a sharp increase occurring in the vicinity of the silanol pK_a value.[27] The effect of pH on EOF for the polymer and exchanger packed capillaries was examined since both the silanols on the capillary wall surface and the polymer exchange sites should influence the EOF. Figure 3 compares the EOF values calculated using acetone as the marker at pH 2.5 and 7.0 for the polymer and ion exchanger packed capillaries. The buffers were 4:1 acetonitrile/aqueous 10 and 30 mM TRIS−TRIS-HCl at pH 2.5 or 7.0. The effect of pH on a C-18 packed capillary (Waters Spherisorb, 3-μm ODS-1 and a 3:7 acetonitrile/aqueous 20 mM NaH_2PO_4, pH 2.5 or 20 mM Na_2HPO_4, pH 7.0 (v/v))buffer and an open tube fused-silica capillary (same buffer conditions) are also included in Figure 3.[14] Although not shown, EOF values for silica-based sulfonated cation exchangers (SCXs), Spherisorb 3-μm propyl SCX, phenyl SCX, and Symmetry SCX, were slightly higher when compared to the ODS-1 for the same pH conditions.[14]

Switching from an acidic to a basic pH almost doubles the EOF for the C-18 packed capillary, while for the polymeric PRP-1 packed capillary, EOF is nearly constant over the pH range. Furthermore, the PRP-1 EOF, which is similar in basic pH, is almost twice the C-18 EOF in acidic solution. The EOFs for the PSDVB ion exchanger packed capillaries (EOFs for all anion exchangers are reversed) undergo only a very small change as pH is varied. The strong acid and base ion exchangers are highly dissociated and should be less sensitive to pH, but even the absence of exchange groups (PRP-1) and the weak base ion exchanger (PRP-X100) (cation form at the pH conditions used) generate EOF values that are nearly pH insensitive. A similar near-constant EOF with pH change was observed for the alkyl/sulfonated modified silica-based cation exchanger packed capillary.[49] For the PSDVB-based cation exchangers, EOF increases with exchange capacity and is slightly higher at the more basic pH. For the anion exchangers, and their reversed EOF, increased exchange capacity provides a more negative EOF and the EOF is slightly less negative at the more basic buffer pH. The small EOF difference between acidic and basic buffer conditions for all the stationary phases is likely due to the EOF contribution of the fused-silica wall silanols as they dissociate from pH 2.5 to 7.0. When the cation exchanger EOF values in Figure 3 are compared to the silica-based cation exchanger EOF values,[14] the polymer-based cation exchangers have larger EOF values. Thus, it can be concluded that the polymeric-based exchangers and their exchange sites have the dominant effect on EOF as suggested previously.[10]

Organic Solvent. Analyte retention and selectivity in CEC is affected by the type and concentration of organic solvent in the buffer similar to solvent effects in HPLC. In addition, the solvent also influences EOF because of the dependence of EOF on dielectric constant and viscosity. Increasing acetonitrile concentration from 50 to 80% in an aqueous pH 7.0, 10−20 mM TRIS−TRIS-HCl (v/v) buffer solution increased EOF in a linear-like fashion for the polymeric adsorbent (PRP-1) and the low- (PRP-X300) and high-capacity cation exchanger (PRP-X400) from 1.31×10^{-4} to 1.94×10^{-4}, 1.58×10^{-4} to 2.17×10^{-4}, and 1.82×10^{-4} to 2.81×10^{-4} cm^2 V^{-1} s^{-1}), respectively. This near-linear change is consistent with other CEC studies with silica-based C-18 and ion exchanger packings.[1,12,23,45,48] The data also indicate that, as exchange capacity increases, EOF increases for a given buffered organic solvent/water ratio. When lower acetonitrile concentrations were used, bubble formation tended to be a problem and for this reason acetonitrile concentrations above 70% were usually used in CEC separations. Using a pressurized CEC system would probably overcome this problem[1−4] and permit lower acetonitrile concentrations, which would have a more significant effect on partitioning of the analytes, to be used with the polymer-based stationary phases.

Figure 4 illustrates the effect of the ratio of acetonitrile/aqueous TRIS−TRIS-HCl, pH 7.0 (v/v) buffer solution at 20 kV on the resolution of a seven-component mixture of neutral analytes that differ in hydrophobicity for a low cation exchange capacity PRP-X300 packed capillary. Resolution of the neutral analytes follows the hydrophobic partitioning characteristic of a reversed-phase interaction. Analyte retention occurs on this packed capillary

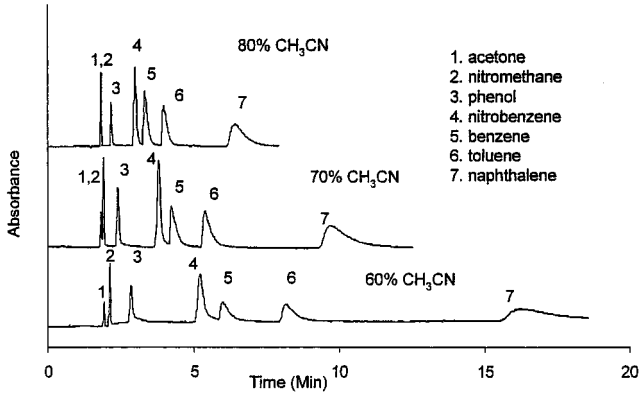

Figure 4. Effect of buffer acetonitrile concentration on migration time and resolution for the separation of EOF markers and aromatic hydrocarbons. Conditions are the same as Figure 1 except for acetonitrile/aqueous buffer ratio.

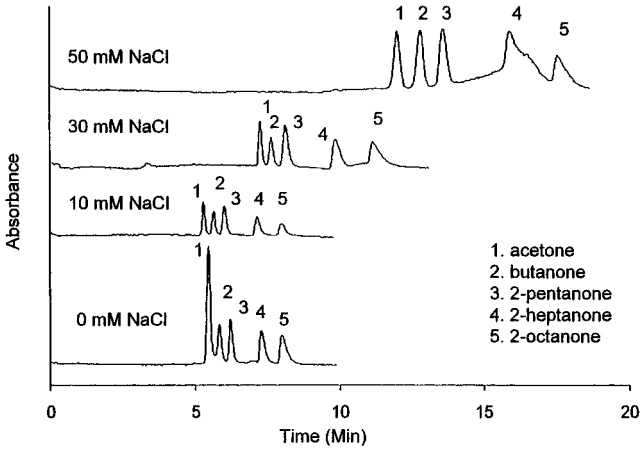

Figure 5. Effect of buffer ionic strength on the migration time and resolution for the separation of short linear alkyl chain methyl ketones. Conditions are the same as Figure 1 except for NaCl concentration and 10 kV.

because the exchange sites are low in number and the polymeric matrix is still available for partitioning. As the acetonitrile concentration increases, analyte partitioning decreases consistent with what would be observed in LC on the polymer-based stationary phases[61] and analyte migration times decrease. Thus, the analyte migration time decrease is due to the combined effect of increased EOF and reduced partitioning. A similar trend was also observed with the alkyl/sulfonated-modified silica-based cation exchanger packed capillary.[49]

Buffer Electrolyte Concentration. EOF in CE decreases as buffer ionic strength is increased because of the effect of the electrolyte on the ζ potential at the silica wall surface. Similarly, in CEC with C-18 packed capillary columns, EOF decreases with increased buffer ionic strength. For example, for a 3.5-μm C-18 packed capillary, EOF decreased by ~39% when the buffer salt concentration was increased from 0 to 60 mM.[10] A decrease in EOF with an increase in ionic strength was also observed in these studies with the PSDVB-based stationary phases. This is illustrated in Figure 5 where a five-component mixture of neutral methyl ketones of simple structure are resolved on a PRP-X300 cation exchanger packed capillary as a function of NaCl concentration in a 4:1 acetonitrile/aqueous 20 mM TRIS−TRIS-HCl, pH 7.0 (v/v) buffer solution. The ketones are retained and resolved due to small differences in their hydrophobicity because of analyte partitioning between the buffer solution and the exchanger polymer matrix as the ketones are electrically driven through the packed capillary. If the exchange sites are eliminated (PRP-1), analyte retention and migration times increase for a given condition. Alternatively, if the number of exchange sites is increased (PRP-X400), retention and migration times are decreased. As NaCl concentration increases from 0 to 50 mM, EOF decreases, based on acetone as the EOF marker, from 1.85×10^{-4} to 0.85×10^{-4} cm^2 V^{-1} s^{-1}. Thus, analyte migration time increases with ionic strength, which also increases resolution.

Stationary-Phase Selectivity/Analyte Structure. Figures 1−5 suggest that the polymer adsorbent- and polymer-based ion exchangers generate reasonable EOF and are capable of providing good selectivity and resolution for mixtures of neutral analytes of simple as well as more complex structures. To further demonstrate this view and to illustrate the retention differences between the stationary phases, an analyte test mixture composed of seven different neutral polar to nonpolar analytes was separated on the seven different polymer and polymer-based exchanger packed capillaries. The buffer was a 4:1 acetonitrile/aqueous 20 mM TRIS−TRIS-Cl, pH 7.0 (v/v) solution and the applied voltage was 20 kV for the reversed-phase adsorbent, PRP-1, and the cation exchangers (see Figure 6A) and −20 kV (polarity is switched because of reversed EOF) for the anion exchangers (see Figure 6B). If 10 and −10 kV are used, respectively, migration times are about 30−40% greater.

Retention order for a test sample of neutral analytes is the same in Figure 6 for PRP-1 and low-capacity ion exchanger packed capillaries. For the high-capacity ion exchangers, which may exhibit normal-phase partitioning, and depending on the buffer composition, retention order can differ for more polar type analytes. Analyte retention and migration times (see Figure 6) depend on the exchange capacity of the stationary-phase particles. When the cation exchanger and the uncharged, reversed-phase PRP-1 packed capillaries are compared, analyte retention and migration times are the highest for PRP-1 as the neutral analytes are electrically driven through the capillaries. As cation exchange capacity increases, analyte retention and migration times decrease because the charged sites interfere in partitioning of the analyte with the polymer matrix. When exchange capacity is large, for example, PRP-X400 in Figure 6A, retention is very low and resolution is lost for the test mixture. This is not due to increased EOF, which occurs with the PRP-X400, but rather is due to reduced retention of the analyte toward the stationary-phase polymeric matrix because of the large number of exchange sites. This prevents the neutral hydrophobic analytes from interacting with the polymeric matrix of the exchanger, and consequently, the neutral analytes migrate through the packed capillary quickly. The highest resolution is thus obtained with the PRP-1 packed capillary, but the more favorable analysis time and peak shapes (modestly increased higher EOF) with still good resolution (modestly lower retention) are obtained with the low cation exchange capacity PRP-X300 packed capillary. For the anion exchanger packed capillaries (Figure 6B), where EOF is reversed and polarity is switched, increasing anion exchange capacity also decreases neutral analyte retention and migration times because the PSDVB matrix becomes less available for partitioning. But,

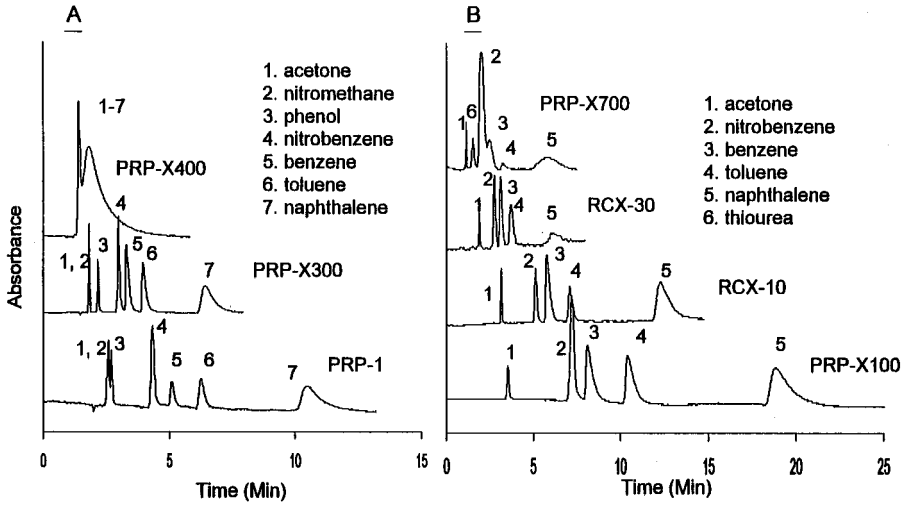

Figure 6. Effect of the PSDVB adsorbent and cation and anion exchanger stationary phases on migration time and resolution. Conditions are the same as Figure 1 except for (B), where the applied voltage is −20 kV.

since the EOF for the low-capacity anion exchanger (PRP-X100) is about half that of the low-capacity cation exchanger (PRP-X300) (see Table 2), neutral analyte migration times on the PRP-X100 are much greater. As exchange capacities of the cation and anion exchangers increase, the difference in analyte migration time between the two disappears because the EOF for the two becomes similar (see Table 2).

Analyte peaks generally have good peak shapes for the low-capacity ion exchanger capillaries but tend to tail for the PRP-1 capillary when analyte retention and migration times are high. This is probably due to mass-transfer effects. When the PRP-1 is used in LC applications, column efficiencies are less than those obtained with typical silica-based C-18 columns because of differences in mass transfer.[61] For Figure 6A, peak efficiency for the nitrobenzene peak is about 2.4×10^4 plates/m for the PRP-1 capillary and 2.1×10^4 plates/m for the PRP-X300 capillary while for the PRP-X100 capillary efficiency for the nitrobenzene peak in Figure 6B is $\sim 2.4 \times 10^4$ plates/m.

A second analyte test mixture composed of seven substituted benzene derivatives that differ in polarity was separated to further demonstrate the effect of analyte structure and stationary-phase properties on retention and migration time and to demonstrate pH stability of the stationary phase. Since EOF is essentially independent of buffer pH, it should be possible to use these packed capillaries at a modestly strong acidic condition without worry about stationary-phase stability. Thus, weak acid analytes would be in their neutral form, if buffer pH is low enough to suppress ionization. Figure 7 lists the CEC electrochromatogram for the substituted benzene derivative separation on a low-capacity cation exchanger, PRP-300, packed capillary at three applied voltages. The buffer was a 4:1 acetonitrile/aqueous 10 mM TRIS−TRIS-Cl, pH 2.5 (v/v) solution. Six of the analytes are neutral; weak acid phenol is also neutral because it is undissociated in the acidic buffer. All seven analytes are baseline resolved, and migration order in Figure 7 is consistent with the hydrophobic properties of the benzene derivatives. For silica-based strong acid cation exchanger packed capillaries,[14] operation below pH 4.5 is not recommended. When the applied voltage is increased (see Figure 7), EOF increases and analyte migration times decrease. Even at 30 kV baseline resolution of the seven-component mixture

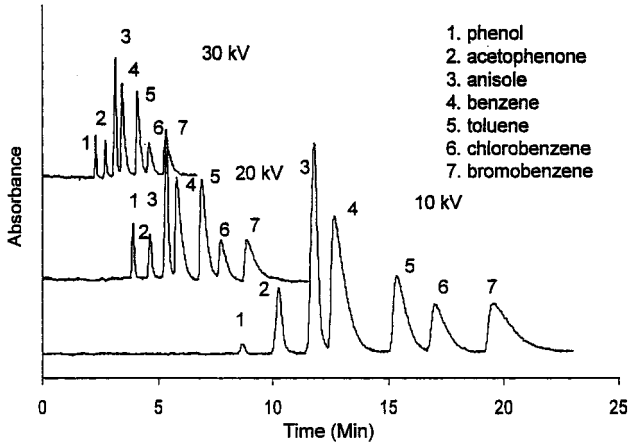

Figure 7. Separation of substituted benzene derivatives on a low-capacity cation exchanger at pH 2.5. Conditions are the same as Figure 1 except the buffer is 10 mM, pH 2.5, and applied voltage is varied.

is obtained and analysis time is reduced to about 7 versus 23 min at 10 kV applied voltage.

The stability of the polymeric-based stationary phases at low pH compared to the silica-based stationary phases is a major advantage. Thus, dissociation of weak acid analytes can be suppressed, which allows their CEC separation as neutral analytes. In addition, weak bases can be converted into cations in a low-pH buffer and are potentially CEC separable with favorable resolution, efficiency, and analysis time. Figure 8 illustrates the separation of linear alkyl chain carboxylic acids from C-2 to C-10 on PRP-1 and low-capacity cation exchanger, PRP-X300, packed capillaries. As analyte carbon chain increases, analyte hydrophobicity increases and retention on the two stationary phases should increase. If the weak acids are undissociated, which is the case in a low-pH buffer, retention and migration time should be even higher. The low-pH background electrolyte solution used in Figure 8 is 7:3 acetonitrile/aqueous 10 mM H_2SO_4 with an applied voltage of 10 kV. This type of acidic pH solution is usually not used with C-18 stationary phases because of poor stability in this kind of environment. Migration order in Figure 8 follows analyte hydrophobicity, and retention and migration times are higher on the

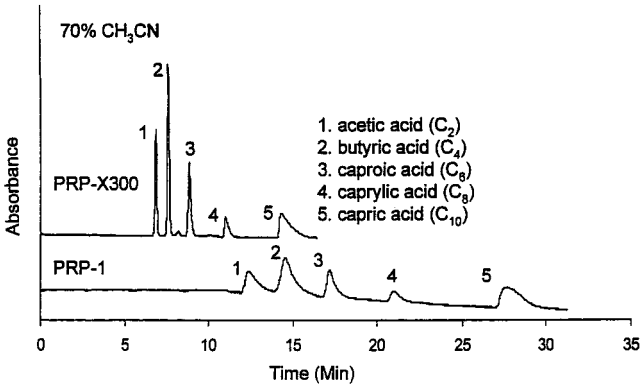

Figure 8. Separation of linear alkyl chain carboxylic acids on a PSDVB adsorbent and low-capacity cation exchanger. Capillary dimensions are the same as Figure 1 and the buffer is 7:3 acetonitrile/aqueous 10 mM H_2SO_4 at 10 kV.

more hydrophobic PRP-1 stationary phase. For the low-capacity strong acid cation exchanger (PRP-X300), analyte migration times are reduced, analysis time is cut almost in half (reduced retention is a more important factor than the slightly increased EOF), and baseline resolution is still obtained. Peak shapes are better defined, peak efficiency for acetic acid and butyric acid is 4.8×10^{-4} and 4.2×10^4 plates/m, respectively, and stationary-phase stability does not appear to be affected by the strong acid conditions.

If acetonitrile concentration in the acidic solution is increased, analyte retention is decreased and is consistent with a reversed-phase type of analyte interaction. For example, at 90% acetonitrile and the PRP-X300 packed capillary, baseline resolution for the five carboxylic acids in Figure 8 is still obtained but analysis time is now ~9 min versus ~17 min for 70% acetonitrile. Increasing the applied voltage can also be used to reduce migration time.

CONCLUSION

CEC studies indicate that a fused-silica capillary packed with a macroporous PSDVB reversed-phase adsorbent or PSDVB-based cation or anion exchangers yield sufficient EOF when an electric field is applied to electrically drive neutral and charged analytes through the capillary. These stationary phases have advantages over silica-based C-18 and ion exchanger stationary phases. The polymer surface is acid and base stable, its surface charge is increased by ion exchange sites, and free silanol sites are absent. Partitioning of analytes in CEC between the buffer solution and polymer surface occurs according to analyte hydrophobic properties which retards analyte movement through the capillary. Even neutral analytes of simple structure, such as acetone, thiourea, and acrylamide, which are frequently used as EOF markers, undergo weak partitioning with the PSDVB-based adsorbents and ion exchangers, making EOF determinations more difficult. EOF increases as organic solvent in the buffer or applied voltage increases and decreases as buffer ionic strength increases. EOF is nearly independent of pH and increases as stationary-phase ion exchange capacity increases. For anion exchangers, EOF is reversed. The number of exchange sites also influences partitioning of the analyte with the polymer matrix; as exchange capacity increases analyte retention and migration time decreases. Thus, control of the exchange capacity becomes an important parameter in determining analysis time for CEC separations. The PSDVB-based adsorbent and ion exchangers as stationary phases for CEC provide good resolving power and efficiency (lower than silica-based C-18 and ion exchangers) and are reproducible and applicable to the separation of a wide range of neutral analytes. Because the PSDVB matrix, unlike a silica matrix, is stable at a low pH and the EOF is also favorable at this condition, the PSDVB-based adsorbent and ion exchangers are useful for the CEC separation of weak acids and weak bases. Weak acids can then be separated as neutral species, since the acidic buffer suppresses ionization. In contrast, weak base analytes can be converted into their cation forms for CEC separation.

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