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Separation of Achiral and Chiral Analytes Using Polymeric Surfactants with Ionic Liquids as Modifiers in Micellar Electrokinetic Chromatography

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In this study, we report the use of ionic liquids as modifiers in the separation of achiral and chiral analytes in micellar electrokinetic chromatography. In this investigation, polymeric surfactants and ionic liquids were added to a low-conducting buffer solution. The polymeric surfactants used in this study were poly(sodium *N*-undecylelinic sulfate) and poly(sodium oleyl-L-leucylvalinate). The ionic liquids used in this study were chosen because of their high conductivity, hydrophobicity, and good solvating properties. Thus, it was expected that these ionic liquids would have the ability to assist in the separation of hydrophobic mixtures while maintaining adequate background current. Three analyte mixtures were separated using various buffer combinations of polymeric surfactant and ionic liquids. The ionic liquids were shown to improve the resolution and peak efficiency of the analytes while maintaining adequate background current.

Ionic liquids (ILs), sometimes called molten salts, are liquids at ambient temperatures and consist entirely of ionic species. In the past, ILs were mainly of interest to electrochemists. However, recently it has become apparent that a wide range of chemical reactions can be conducted using this class of solvents.[1] For example, many recent scientific investigations have focused on ILs[2−29] as a new class of solvents for various chemical reactions, such as liquid−liquid extraction,[5,6] organic synthesis,[7−12] electrochemistry,[13−16] catalysis for clean technology,[17−21] ultralow volatility liquid matrixes for matrix-assisted laser desorption/ionization (MALDI) mass spectrometry,[22] and separations.[23−27]

The typical ionic liquid consists of a bulky pyridinium or imidazolium cation paired with a variety of anions.[3,13,14] Ionic liquids have many properties of conventional organic solvents, such as excellent solvation qualities, a low viscosity, and a wide temperature range.[3,16−18] Two characteristics that ILs do not share with conventional organic solvents are volatility and good electrical conductivities.[3,4,7,16] Ionic liquids are environmentally benign, nonvolatile, and nonflammable with a high thermal stability.[4] Their miscibility in water is heavily dependent on the type of anion forming the ionic liquid. In addition, the length of the alkyl chain on the pyridinium or imidazolium cation has a considerable effect on the properties of the ionic liquid.[19] Wilkes and Zaworotko[7] concluded that the l-ethyl-3-methylimidazolium (EMIM) cation was chemically and electrochemically robust and was generally useful for synthesis of ionic liquids. Fuller and co-workers[28] fully characterized the low-melting salt, l-ethyl-3-methylimidazolium hexafluorophosphate (EMIMPF$_6$, mp 58−60 °C) and concluded

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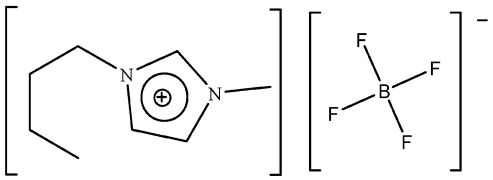
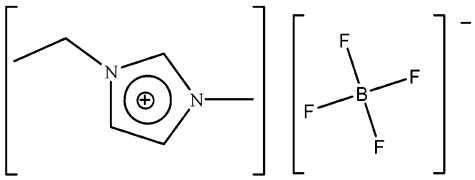


1- butyl-3-methylimidazolium
tetrafluoroborate ($BMIMBF_4$)



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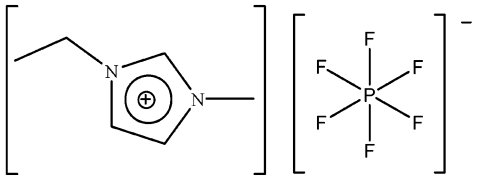
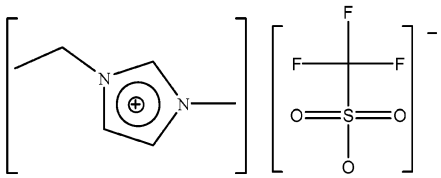
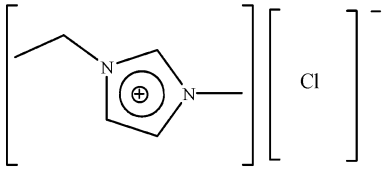


1-ethyl-3-methylimidazolium
hexafluorophosphate ($EMIMPF_6$)



1-ethyl-3-methylimidazolium
Trifluoromethanesulfonate ($EMIMSO_3F_3$)



1-ethyl-3-methylimidazolium
Chloride (EMIMCl)

Figure 1. Chemical structures of the ionic liquids (ILs) used as modifiers in the MEKC separation experiments.

that $EMIMPF_6$ interionic interactions were dominated by cation−anion Coulombic attraction with minimal hydrogen bonding. The ionic liquid l-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$, mp 15 °C) was found to be a liquid at room temperature and was highly miscible in water.[26,29]

In addition to the characterization work mentioned above, Armstrong et al. recently developed a solvation model for ionic liquids based on multiple solvation interactions.[4] They concluded that ionic liquids were complex solvent systems, as compared to conventional organic solvents. Using the solvation model, Armstrong and co-workers were able to show that the anion had greater effect on the hydrogen bond basicity of the ionic liquid, as compared to the cation.

The application of ILs for the separation of various classes of compounds has also been recently recognized. Yanes et al. reported the development of a fairly robust capillary electrophoresis (CE) method for the separation of polyphenols found in grape seed extracts in which the IL tetraethylammonium tetrafluroborate was used as the only background electrolyte (BGE).[25] More recently, Yanes and co-workers developed a CE method for the same analysis using 1-ethyl-3-methylimidazolium-based ionic liquids as the BGE.[26] In another publication, Armstrong et al. examined two ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) and 1-butyl-3-methylimidazolium-chloride (BMIMCl)) as stationary phases in gas−liquid chromatography.[27]

In micellar electrokinetic chromatography (MEKC), a surfactant is added into the buffer to separate either chiral or achiral analytes. The use of polymeric surfactants bearing both chiral and achiral ionic headgroups has been reported.[30−33] In some cases, organic modifiers have been used in the separation of hydrophobic environmental pollutants, such as polycyclic aromatic hydrocarbons (PAHs), and alkyl aryl ketones, to help resolve such mixtures.[33,34] To date, the use of ionic liquids as modifiers in MEKC using polymeric surfactants has not been investigated. When using ionic liquids, the choice of the BGE is very important, because most ionic liquids are highly conductive. There are several advantages for using ionic liquids over organic solvents as modifiers. Ionic liquids are soluble in water, have a good electrical conductivity, and act as good electrolytes in CE either when used independently or when mixed with other buffers. Ionic liquids are slightly more viscous than organic solvents; therefore, low concentrations may be required for buffer modifications to achieve better separations. In addition, ionic liquids are less volatile and are referred to as "green solvents", meaning they are environmentally friendly. In contrast, organic solvents are poor conductors of electricity, and high concentrations of organic solvents in the buffer cause current breakdowns in CE. In addition, most organic solvents are highly volatile and harmful to the environment.

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In this paper, ionic liquids were used as modifiers in micellar electrokinetic chromatography (MEKC) using polymeric surfactants to separate both achiral and chiral compounds. The ionic liquids used in this study were 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$), l-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$), l-ethyl-3-methylimidazolium hexafluorophosphate ($EMIMPF_6$), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ($EMIMSO_3F_3$), and 1-ethyl-3-methylimidazolium chloride (EMIMCl); their chemical structures are shown in Figure 1. Three different analyte mixtures were separated using these ionic liquids. Those mixtures included a mixture of eight alkyl aryl ketones, a mixture of seven phenols, and a mixture of three chiral binaphthyl derivatives. The performance of sodium dodecyl sulfate (SDS) with the ionic liquids was compared to that of poly-SUS with the ionic liquids for the separation of alkyl aryl ketone mixture.

EXPERIMENTAL SECTION

Materials. The alkyl aryl ketones (acetophenone, propiophenone, butyrophenone, valerophenone, hexanophenone, heptanophenone, octanophenone, decanophenone, and dodecanophenone) the phenols (4-chlorophenol, 3-chlorophenol, 4-chloro-3-methylphenol, 2-chlorophenol, 2,4,6-trichlorophenol, 2,4-dichlorophenol, and pentachlorophenol), and the chiral compounds ((±)-1,1′-bi-2-naphthol (BOH), (±)-1,1′-bi-2-naphthyl-2,2′-diyl hydrogen phosphate (BNP), and 1,1′-bi-2-naphthyl-2,2′-diamine (BNA)) were purchased from Sigma-Aldrich (Milwaukee, WI) (Figure 2). The undecylenyl alcohol, sodium borate, chlorosulfonic acid, pyridine, oleic acid *N*-hydroxysuccinimide ester, sodium hydrogen carbonate, sodium borate, disodium phosphate, tris(hydroxymethyl)aminomethane (TRIS), tetrahydrofuran (THF), sodium dodecyl sulfate (SDS), and the ionic liquids $EMIMBF_4$, $EMIMPF_6$, $EMIMSO_3F_3$, and EMIMCl were also obtained from Sigma-Aldrich. The ionic liquid $BMIMBF_4$ was purchased from Chemada Fine Chemicals Ltd., (Nir Itzhak, D.N.HaNegev 85455, Israel). The dipeptide leucine−valine was purchased from Bachem Bioscience Inc (King of Prussia, PA). All reagents were of analytical grade and were used as received without further purification.

Synthesis of Poly(sodium *N*-undecylelinic sulfate) [Poly-(SUS)]. The sodium undecylinic sulfate (SUS) monomer was prepared according to Bregstrom's procedure,[35] and modifications were made according to the procedure described by Shamsi et al.[34] to obtain the polymerized surfactant poly-SUS.

Synthesis of Poly(sodium oleyl-L-leucylvalinate) [Poly-(L-SOLV)]. The L-SOLV monomer and polymer poly-L-SOLV were synthesized using the guidelines of the procedure reported by Wang and Warner,[36] with some modifications as described in a previous study.[37] All polymers used in this study were found to be >99% pure as estimated by elemental analysis.

Preparation of MEKC Buffer Solutions. The background electrolyte (BGE) used for separation of the alkyl aryl ketones was 100 mM TRIS at pH 10, and the BGE used for the phenols was 20 mM sodium borate and disodium phosphate at pH 9.2. The BGE used for the binaphthyl derivatives was 100 mM TRIS mixed with 10 mM sodium borate at pH 10. The pH of the BGE was adjusted with 1 M NaOH or 1 M HCl, whenever was necessary. An appropriate amount of the polymeric surfactant was then added to the BGE. The ionic liquid was then added as a modifier to examine the separation efficiency and resolution of the analytes.

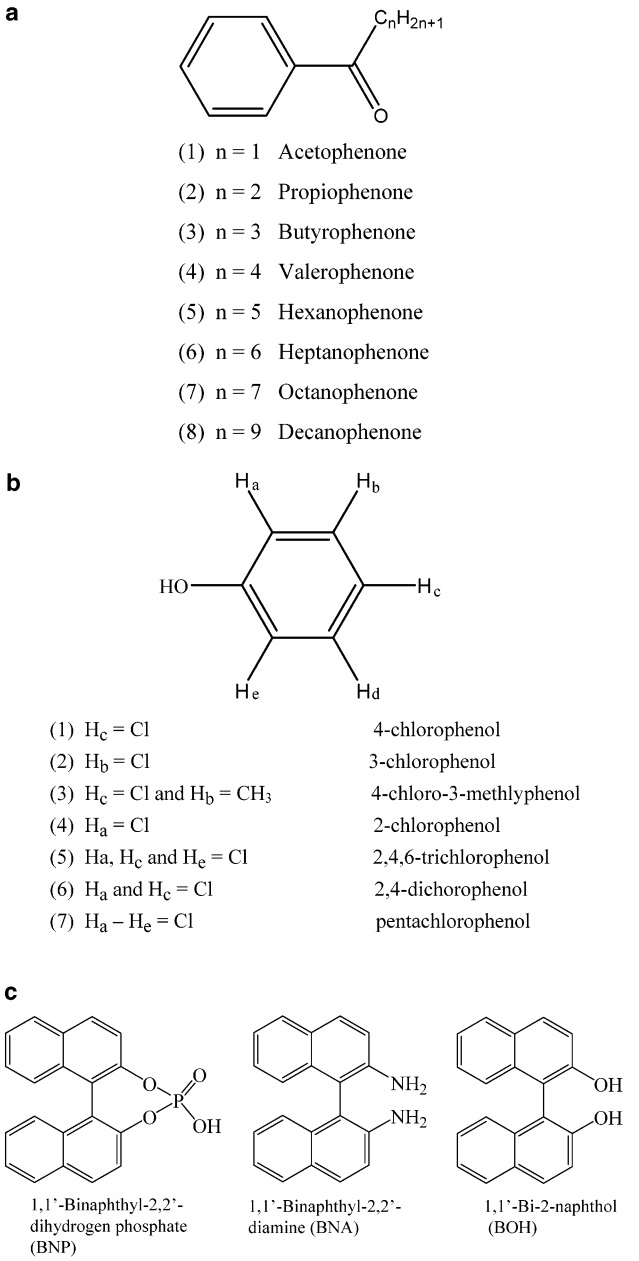

Figure 2. (a) Chemical structures of the eight alkyl aryl ketones. The elution order is 1−8, except where peaks are coeluting. (b) Chemical structures of the seven phenols. The elution order is 1−7, except where peaks are coeluting. (c) Chemical structures of the three chiral binaphthyl derivatives.

Capillary Electrophoresis. The MEKC experiments were performed by use of a Hewlett-Packard 3D CE instrument (Foster city, CA) equipped with a UV diode array detector. Bare fused-silica capillaries (effective length 40 cm, 50-μm i.d. for the separation of the ketones and phenols compounds and effective length 52 cm, 50-μm i.d. for the separation of the binaphthyl compounds), were purchased from Polymicro Technologies

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(Phoenix, AZ). The applied voltage ranged from +20 to +30 kV. The detection wavelength was 254 nm. The temperature of the capillary was maintained at 20 °C for the alkyl aryl ketones and phenols and at 15 °C for the binaphthyl derivatives by the instrument thermostating system, which consisted of a peltier element for forced-air cooling and temperature control. Different capillary temperatures were chosen for the achiral and chiral analyte separation in order to strictly optimize the separations.

The binaphthyl derivatives were prepared in 50:50 methanol/water at concentrations of 0.1 mg/mL. The ketones and the phenols were prepared in methanol at a concentration of 0.1 mg/mL. The samples injection size varied from 50 mbar for 1 s to 30 mbar for 3 s. Prior to use, each new capillary was conditioned for 30 min with 1 M NaOH and then for 30 min with 0.1 M NaOH. Finally, the capillary was rinsed for 15 min with triply distilled deionized water. Prior to each run, the capillary was flushed with MEKC buffer for 3 min to condition and fill the capillary. To change from one buffer to another (i.e., buffer containing poly-SUS and an ionic liquid to another buffer containing poly-SUS and a different ionic liquid), the capillary was flushed with 0.1 M NaOH for 10 min and rinsed with water for 5 min, then filled with the new MEKC buffer containing the ionic liquid for 5 min. This was done to minimize any influence of the previous buffer.

Calculations. The retention factors for two of the analytes (i.e., acetophenone and decanophenone were determined using eq 1,[38]

$$k = \frac{(t_r - t_{eo})}{t_{eo}(1 - t_r/t_{mc})} \quad (1)$$

where t_{eo} is the migration time of an unretained solute, t_r is the retention of a solute, and t_{mc} is the migration of the micelle or polymeric surfactant. Methanol was used as the electroosmotic flow (t_{eo}) marker and was measured from the time of injection to the first deviation from baseline. The migration time of the micelle or polymeric surfactant (t_{mc}) was determined using *n*-dodecaphenone as the marker. The resolution of the chiral analytes was calculated using eq 2, [39]

$$R_s = 2\,\frac{(t_{r2} - t_{r1})}{w_1 + w_2} \quad (2)$$

where t_{r1} and t_{r2} are the respective migration times of each enantiomer, and w_1 and w_2 are the peak widths at the baseline of each enantiomer.

RESULTS AND DISCUSSION

Separation of Alkyl Aryl Ketones. Experiments were conducted to separate a mixture of eight alkyl aryl ketones, first using SDS, and later poly-SUS in the buffer. The separation results obtained at the optimized buffer pH, voltage, temperature, and SDS concentration are illustrated in Figure 3 I. Only five out of the eight alky aryl ketones in the mixture were resolved. The elution order for these ketones was from the least hydrophobic analyte acetophenone ($n = 1$) to the most hydrophobic analyte decanophenone ($n = 9$). The peak numbers are based on the labeling used for Figure 2a. The optimized SDS concentration was 50 mM. Higher concentrations of SDS led to poor resolution and longer migration times of the analytes, but lower concentrations of SDS did not enhance the separation.

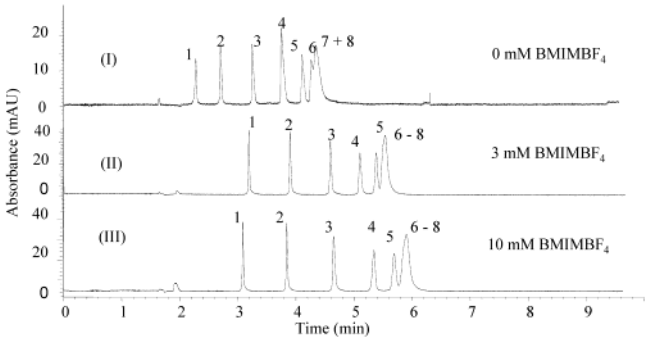

Figure 3. Electropherograms showing the separation of eight alkyl aryl ketones: (I) using 50 mM SDS, (II) using 50 mM SDS + 3 mM $BMIMBF_4$, and (III) using 50 μM SDS + 10 mM $BMIMBF_4$. Conditions: 100 mM TRIS buffer, pH 10.0, press. Injection, 50 mbar for 1 s; temp, 20 °C; voltage, 30 kV; detection λ, 254 nm.

To enhance the resolution of the analytes, ILs were used as modifiers using the SDS optimized concentration (50 mM). The UV studies showed that the ionic liquid had a strong absorbance in the region between 215 and 235 nm (data not shown). An ionic liquid concentration study was done using 1−10 mM of each ionic liquid in order to determine the optimum amount to be added to the MEKC buffer composed of 50 mM SDS and 100 mM TRIS at pH 10. Figure 3 electropherograms II and III are representative of the data obtained when ionic liquids were used as modifiers using SDS as the pseudostationary phase. The ionic liquids increased the migration time of the analytes but did not enhance either the resolution or the efficiency for SDS separations of these compounds.

The separation of the eight alkyl aryl ketones mixture was also done using poly-SUS. The poly-SUS concentration and separation conditions were optimized. The MEKC buffer consisted of 0.5% poly-SUS and 100 mM TRIS at pH 10. Figure 4a I shows that a better separation was achieved using poly-SUS than SDS for the separation of the alkyl aryl ketones mixture. Six out of the eight alkyl aryl ketones were well-resolved and eluted in <10 minutes. However, the last three analytes coeluted. Of the five ionic liquids used as modifiers in the MEKC buffer, $BMIMBF_4$ gave the best results. Figure 4a II−VII illustrates the effect of $BMIMBF_4$ concentration on the separation of the ketone mixture. The elution order was determined by spiking a small amount of each analyte into the mixture, and the peaks are numbered according to the analyte notation in Figure 2a. Slight changes in the EOF as well as the migration times of the first four analytes when the concentration of $BMIMBF_4$ was increased from 1 mM to 5 mM were observed. However, the peak efficiencies and resolution of these analytes were almost maintained. Shorter migration times of the last four analytes were observed as the concentration of $BMIMBF_4$ was increased from 0 to 2 mM. However, longer migration times were observed for $BMIMBF_4$ concentrations >2 mM. This trend is observed by viewing the plot of capacity factor (k') of the least hydrophobic analyte acetophenone ($n = 1$) and the most hydrophobic analyte decanophenone ($n = 9$) versus the concentration of $BMIMBF_4$, as shown in Figure 4b. The other

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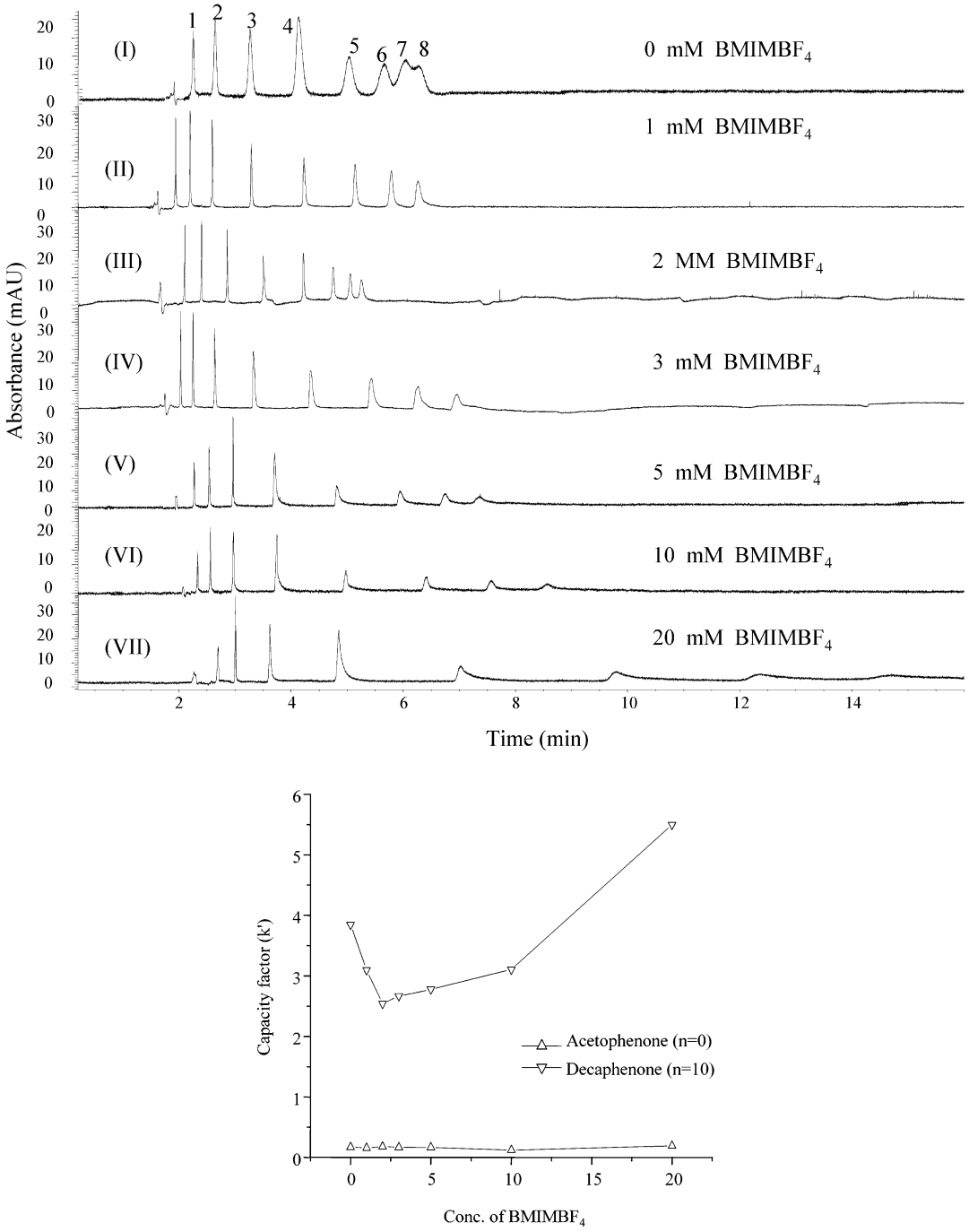

Figure 4. (a) Electropherograms showing the separation of eight alkyl aryl ketones: (I) no modifier; (II−VII) using 1, 2, 3, 5, 10, and 20 mM $BMIMBF_4$ as modifiers. Conditions: 0.5% poly-SUS, 100 mM TRIS buffer, pH 10.0. Pressure injection, 50 mbar for 1 s; temp, 20 °C; voltage, 30 kV; detection λ, 254 nm. (b) Plot of capacity factor (k') of the least hydrophobic and first analyte to elute (acetophenone) and the most hydrophobic and last analyte to elute (decanophenone) versus the concentration of $BMIMBF_4$.

ILs, $EMIMSO_3F_3$ and EMIMCl, were used as modifiers in the separation of alkyl aryl ketones, but the separation was not enhanced.

Hydrophobic solutes are known to partition between the aqueous phase and the polymeric pseudostationary phase in MEKC. Because of their hydrophobicity, the alkyl aryl ketones are retained in the polymeric pseudostationary phase more than the aqueous phase. Figure 4a I shows that decanophenone (n = 9) interacts more with the polymeric pseudostationary phase. ILs are conductive; thus, an addition of an IL to a buffer may enhance its ionic strength under a controlled capillary temperature. This fact was confirmed by an increment in the current as the concentration of $BMIMBF_4$ was increased in the buffer, as shown in Figure 5. Other parameters held constant. An enhancement in the ionic strength or concentration of the background electrolyte is expected to cause the "value" of EOF to decrease and results in an increase in the migration time of the analytes being separated. However, in looking at Figure 5, an abnormality in the EOF versus BMIMBF4 concentration plot is observed. Between 1 and 2 mM, the value of EOF increases with an increase in the

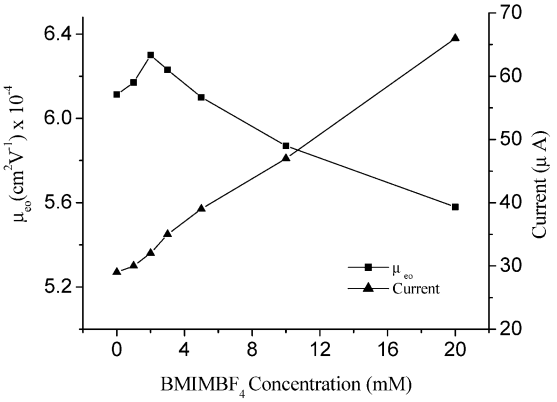

Figure 5. Effect of increasing 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) concentration on the eletroosmotic flow (EOF) and the observed current for the separations in Figure 4a.

concentration of the ionic liquid. A plausible explanation given for this trend is that, when 1−2 mM of the IL were added to the buffer, we observed an increase in the value of EOF as a result of an enhancement in the current, as shown in Figure 5. It was assumed that low concentrations of the ionic liquid caused a compression of the mobile layer, making the value of EOF increase. However, the addition of 3 mM or more of the IL in the buffer led to a decrease in the value of EOF, although we observed an enhancement in current. This is because at higher concentrations of the IL, the (BMIM) cation is likely to coat the capillary wall. Modification of the capillary wall by the IL cation may lead to a change in the EOF. Yanes et al. illustrated that when the ionic liquid was used as an electrolyte, it attached to the capillary wall, engendering anodic EOF.[26] In our case, the TRIS buffer was

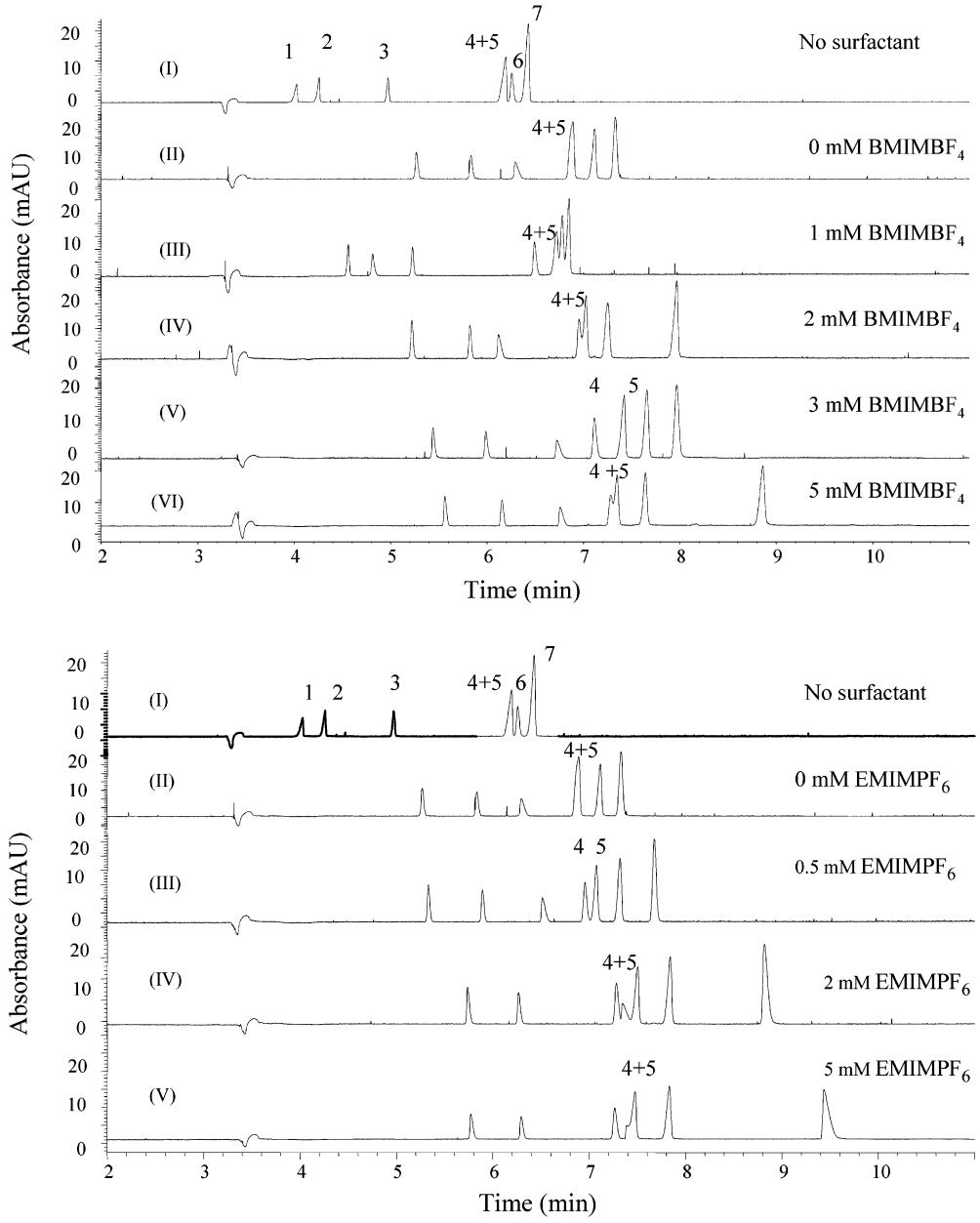

Figure 6. (a) Electropherograms showing the separation of seven phenols: (I) no surfactant; (II) 0.5% poly-SUS; (III), (IV), (V), and (VI) using 0.5% poly-SUS with 1, 2, 3, and 5 mM $BMIMBF_4$, respectively. Conditions: 20 mM $Na_2B_4O_7/Na_2HPO_4$, pH 9.2. Voltage, 20 kV; temp, 20 °C; injection size, 30 mbar for 3 s; and detection λ, 254 nm. (b) Electropherograms showing the separation of seven phenols: (I) no surfactant; (II) 0.5% poly-SUS; (III), (IV), and (V) using 0.5% poly-SUS with 0.5, 2, and 5 mM $EMIMPF_6$, respectively. Conditions same as in Figure 6a.

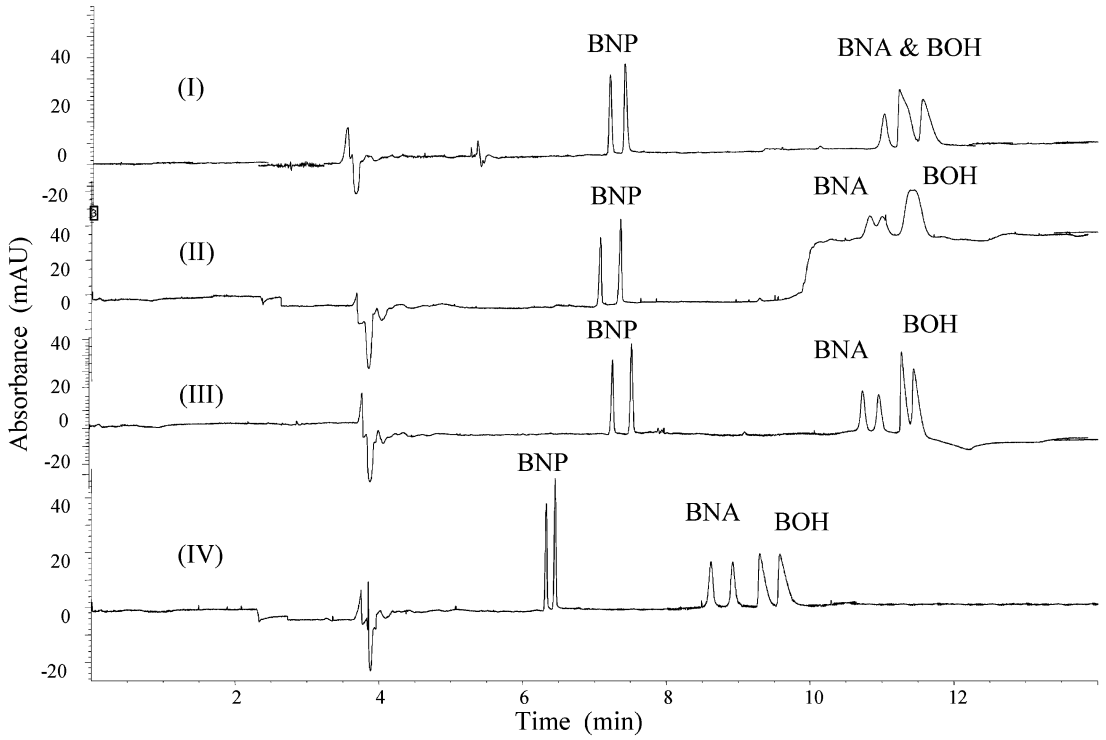

Figure 7. Electropherograms showing the separation of three binaphthyl derivatives using (I) no modifier, (II) 5 mM $EMIMPF_6$, (III) 1 mM $BMIMBF_4$, and (IV) 2 mM $EMIMBF_4$ as modifiers. Conditions: 0.5% poly-L-SOLV, 100 mM TRIS + 10 mM sodium borate buffer, pH 10.0. Press. Injection, 30 mbar for 3 s; temp, 15 °C; voltage, 30 kV; and detection λ, 254 nm.

responsible for the cathodic EOF. The addition of 1−2 mM of $BMIMBF_4$ led to an increase in the current and a slight increase in the EOF, which in turn led to shorter migration times and an enhancement in the peak efficiency, especially the last three analytes. At this low concentration of the ionic liquid, we suppose that the ionic liquid cation moves with the buffer rather than coating on the capillary wall. However, with the addition of 3 mM or higher of $BMIMBF_4$, a reasonable amount of coating of the cation on the capillary wall is possible, which causes a decrease in the EOF value and leads to longer migration times as well as poor peak efficiency of the more hydrophobic analytes, although we observed an enhancement in the current. Ionic liquids are complex solvent systems and the mechanism of separation when ionic liquids are used as modifiers in MEKC is still not well-understood. We are carrying out further studies, which involve separating more hydrophobic analytes, such as PAHs, and using fluorescence spectroscopy and other techniques to achieve a better understanding of the interactions between ILs, polymeric surfactants, and the analytes of interest.

Separation of Phenols. Seven chlorophenols were separated using a plain buffer (i.e., 20 mM $Na_2B_4O_7/Na_2HPO_4$, pH 9.2), buffer + poly-SUS, and buffer + poly-SUS + ILs. The results recorded while using the plain buffer are shown in electropherogram I of Figure 6a,b. Six out of seven of the analytes were well-resolved but peaks 4 and 5 (i.e., 2-chlorophenol and 2,4,6-trichlorophenol) coeluted. The separation of the phenols was possible even with plain buffer because the phenols are slightly charged at pH 9.2 used in this study.

Poly-SUS was then added to the buffer to enhance the separation of the phenols, and the corresponding data is shown in electropherogram II in Figure 6a,b. The presence of the surfactant increased the elution time of the analytes and gave a better resolution of the six analytes, as compared to that achieved with the plain buffer. The ILs were used in order to improve the resolution of peaks 4 and 5. Of the five ILs investigated, only$BMIMBF_4$ and $EMIMPF_6$ enhanced the resolution of the peaks, as shown in electropherogram V, Figure 6a, and electropherogram III, Figure 6b, respectively. A similar trend was observed for the migration times of the phenols as with the alkyl aryl ketones when the IL $BMIMBF_4$ was used as the modifier. When $EMIMBF_4$, $EMIMSO_3F_3$, and EMIMCl were used as modifiers, longer migration times of the analytes were recorded, although there were no significant changes in the EOF. In addition, the coeluting peaks (4 and 5) were not resolved (data not shown).

Enantiomeric Separation of Binaphthyl Derivatives. The binaphthyl derivatives examined in this study were BNP, BOH, and BNA. These analytes have been separated in our laboratory using different chiral surfactants.[40,41] The chirality of the binaphthyl derivatives is attributed to the chiral plane (C_2 symmetry). This group of compounds has a varying degree of hydrophobicity and charge states under the experimental conditions used in this work. Using poly-L-SOLV surfactant in a 100 mM TRIS 10 mM sodium borate buffer (MEKC buffer), the *S* and *R* enantiomers of each chiral analyte could only be resolved individually, not in a mixture. The separation was also examined when ILs were added to the MEKC buffer. Electropherogram I in Figure 7 shows that BNA and BOH coeluted in the absence of an IL in the MEKC buffer, whereas electropherograms II, III, and IV are a display of the data collected when the optimized concentration of three different ionic liquids $EMIMPF_6$, $BMIMBF_4$, and $EMIMBF_4$, respectively, were added to the MEKC

Table 1. Resolution Values of the Binaphthyl Derivatives Separated in Figure 6 under the Optimized Concentrations of $EMIMPF_6$, $BMIMBF_4$, and $EMIMBF_4$

electropherogram no. in Figure 6	amt, type of modifier	BNP resolution	BNA resolution	BOH resolution
I	0 mM	3.28		
II	5 mM $EMIMPF_6$	5.03	0.67	
III	1 mM $BMIMBF_4$	4.51	2.03	1.28
IV	3 mM $EMIMBF_4$	2.97	2.95	1.76

buffer. The migration times of the analytes varied depending on the IL used. $EMIMPF_6$ provided enhanced separation of all three analytes. However, no enantiomeric separation was observed for BOH, as shown in Figure 7 electropherogram II. A shift in the baseline was observed for this separation. The cause of this shift was not completely discernible but it could be responsible for the poor enantiomeric separation of BNA and BOH. Both $BMIMBF_4$ and $EMIMPF_6$ facilitated the separation of all three chiral compounds with baseline resolution of the *R* (+) and *S* (−) enantiomers for each compound. The enantiomeric recognition was, however, based on the interactions of the analytes with the chiral poly-L-SOLV surfactant. The resolutions of each analyte under each different buffer solution are recorded in Table 1.

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CONCLUSIONS

Successful separations of two achiral mixtures and one chiral mixture have been achieved using ILs as pseudostationary phase modifiers. The results obtained were reproducible, and the ILs were found to be stable in the background electrolyte solutions. The separation of the analyte mixtures was dependent on the interaction of the analytes with the polymeric surfactants, whereas the ionic liquids influenced the analytes' elution time and peak efficiency. Longer migration times of the more hydrophobic analytes were recorded when high concentrations of the ILs were used as modifiers.

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