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Capillary electrophoretic and nuclear magnetic resonance studies of interactions between halophenols and ionic liquid or tetraalkylammonium cations

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Abstract

Aqueous capillary electrophoretic studies were performed to investigate interactions between halophenols and 1-ethyl-3-methylimidazolium tetrafluoroborate or tetraethylammonium tetrafluoroborate electrolytes. In both cases, increased halogen size correlated with increased affinity for the electrolyte cation. For isomers, the ortho substituted isomer exhibited higher affinity than the para isomer. Irreproducible CE results for analyte pairs in the presence of the ionic liquid stimulated investigations of the interactions between halophenols as well as with the cations of the electrolyte. These interactions were explored by proton and fluorine one-dimensional NMR. The NMR results indicated differences in the interactions between tetraethylammonium/iodophenols and imidazolium/iodophenols. The NMR results indicate hydrophobic stacking interactions between the iodophenols and possible similar interaction among phenols and imidazolium.

Keywords: Nuclear magnetic resonance; Ionic liquid; Halogenated compounds; Phenols

1. Introduction

Ionic liquids are ionic substances with melting points at room temperature or close to it. They are good solvents for a wide range of materials and have been investigated as solvent replacements for volatile solvents traditionally used in liquid–liquid extraction [1–7]. Since ionic liquids do not have significant vapor pressure, they are considered environmentally benign [1,8]. Typically, ionic liquids are based on imidazolium or other heterocyclic aromatic cations but can be also based on quaternary ammonium ions [9]. The change in anion provides variable viscosity depending on applications as in the case of dicyanamides [10].

The investigation of ionic liquids applied to separations has been diverse. For example, dialkylimidazolium-based ionic liquids were used as electrolytes in nonaqueous capillary electrophoresis (CE) for the separation of phenols and aromatic acids [11]. In another study, 1-alkyl-3-methylimidazolium based ionic liquids as the sole

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electrolyte enabled the capillary electrophoretic separation of the phenolic constituents of grape seed extract [12]. Some ionic liquids have also been used as matrix-assisted laser desorption ionization (MALDI) matrices [13]. The properties of ionic liquids were also investigated as stationary phases for gas chromatography [14].

Halogenated compounds are synthesized in industry and agrochemistry. Many biodegradation products of various chemicals used in industry can contain fluorinated compounds [15]. Chlorinated phenols occur in drinking water as a by-product of the chlorination disinfection processes as well as degradation of hexachlorocyclohexane and chlorobenzenes [16]. They are pollutants of waters and soils [17–19]. In particular, 2-chlorophenol is listed among the top eleven priority pollutants by the US Environmental Protection Agency [20]. The separation of positional isomers of chlorophenols by CE has been investigated using five different volatile electrolytes in the work of Jauregi et al. [21]. Bromophenols are used as flame retardants in TV casing materials and printed circuit boards [22]. Bromophenols also occur widely in the marine environment and have been identified as the compounds responsible for iodoform-like off flavors in prawns and shrimp [23,24].

The aim of this work was to investigate the CE behavior of monohalogenated phenols in the presence of 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]) and compare the results obtained with tetraethylammonium tetrafluoroborate ([NEt_4][BF_4]) because good results were obtained for polyphenolic compounds using these two electrolytes in CE [12,25]. CE reproducibility issues when using [emim][BF_4], stimulated additional nuclear magnetic resonance (NMR) titration studies.

2. Experimental

2.1. Chemicals and reagents

The analytes, 2-fluorophenol (2-FP), 3-fluorophenol (3-FP), 4-fluorophenol (4-FP), 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2-bromophenol (2-BP), 3-bromophenol (3-BP), 4-bromophenol (4-BP), 2-iodophenol (2-IP), 3-iodophenol (3-IP), and 4-iodophenol (4-IP)) and [$^2H_3$]methyl [^{2}H]alcohol were purchased from Aldrich (Milwaukee, WI, USA). Deuterium oxide was obtained from Cambridge Isotope Labs. (Andover, MA, USA). Nitromethane, tetramethylammonium chloride, sodium hydroxide, methanol and potassium hexafluorophosphate were purchased from Fisher Scientific (Fair Lawn, NJ, USA). The 1-ethyl-3-methylimidazolium tetrafluoroborate was provided by The QUILL Centre, Queen's University of Belfast (Belfast, UK). Tetraethylammonium tetrafluoroborate was obtained from Southwestern Analytical Chemicals (Austin, TX, USA).

2.2. CE experimental section

For CE experiments, a 200-m*M* [NEt_4][BF_4] electrolyte solution or a 150-m*M* [emim][BF_4] solution prepared in deionized water was used. All phenol solutions were prepared in methanol. For the electrophoretic runs, the sample solution was diluted with the background electrolyte in a ratio of 100 to 500 μl. The applied voltage was 15 kV; anodic detection was achieved at 240 nm by UV detection. An uncoated silica capillary was used [40 cm (35.4 cm to detector×50 μm I.D.). The capillary temperature was 20 °C. It was conditioned by rinsing with 0.5 *M* sodium hydroxide for 10 min. Then it was cleaned with deionized water for 10 min and rinsed with electrolyte solution for 10 min. Between the runs, the capillary was flushed for 40 s with electrolyte solution. Nitromethane was used as the neutral marker. The CE experiments were conducted on a Bio-Rad BioFocus 2000 capillary electrophoresis system (Bio-Rad Labs., Hercules, CA, USA).

2.3. NMR experimental section

Experiments were performed using a Bruker 400 MHz instrument. Samples were held at constant temperature at 25±0.1 °C and were allowed to equilibrate for 15 min before signal acquisition. Internal standards were used for all experiments to compensate for changes in environment and concentration. The use of tetramethylsilane was problematic in this system because experiments were performed in ^2H_2O. Thus, tetramethylammonium chloride (TMA-Cl) was used as the internal standard.

Invariance in chemical shift for the methyl and ethyl protons of imidazolium confirmed TMA-Cl as a good internal standard.

For ^{1}H NMR, a 30-μl aliquot of 5 m*M* tetramethylammonium chloride (TMA-Cl) solution in $^{2}H_2O$ was used as internal standard and its chemical shift set at 3.0 ppm; for ^{19}F NMR, a 30-μl aliquot of 260 m*M* potassium hexafluorophosphate (KPF_6) solution in $^{2}H_2O$ was used as the internal standard and its chemical shift was set at 0.0 ppm. The [emim][BF_4] and [NEt_4][BF_4] solutions of varying concentration were prepared in $^{2}H_2O$ as well. Solutions of 0.13 *M* 2-IP and 0.13 *M* 4-IP were prepared in methanol.

3. Results and discussion

3.1. CE results

For [NEt_4][BF_4], the 200-m*M* concentration was chosen based on a previous report [25]. For [emim][BF_4], the 150-m*M* concentration was chosen based on results of another previous report [12]. For the [emim][BF_4] solution, the pH was 3.4 and for [NEt_4][BF_4], the pH was 4; however, it should be noted that the electroosmotic flow (EOF) in these electrolyte systems is pH independent as reported previously [12,25]. The electrophoretic mobilities of all the halogenated phenols used in this study were obtained using either [NEt_4][BF_4] or [emim][BF_4]. Electrophoretic mobilities of the analytes were calculated using the formula:

$$\mu_{ep} = \mu_{meas} - \mu_{EOF}$$

where μ_{meas} is the apparent mobility of the analyte. Analytes migrating after neutral marker were assigned negative electrophoretic mobilities.

The electrophoretic mobilities of analytes in [NEt_4][BF_4] and [emim][BF_4] are presented in Table 1. As can be seen from Table 1, the mobilities of fluorophenols in both electrolytes are too close to achieve separations. The biggest differences in mobilities were observed for the iodophenols and bromophenols, which were also seen in the electropherograms of solute pairs. Typical electropherograms are shown in Fig. 1a and b.

Both electrolytes enabled separations of 2-BP and 4-BP, 2-IP and 4-IP, 2-IP and 3-IP and partial separation of 2-CP and 4-CP. In addition, [NEt_4][BF_4] was able to separate 2-BP and 3-BP. It was also possible to separate halophenols with different substituents at the same site.

Table 1
Mobilities of halogenated phenols in 200 m*M* [NEt_4][BF_4] and in 150 m*M* [emim][BF4]

Analyte	μ_{ep} in [NEt4][BF4] -(10^{-4} cm^2 V^{-1} s^{-1})	μ_{ep} in [emin][BF4] -(10^{-4} cm^2 V^{-1} s^{-1})
2-FP	0.27	0.24
3-FP	0.27	0.24
4-FP	0.25	0.23
2-CP	0.38	0.33
3-CP	0.34	0.32
4-CP	0.32	0.29
2-BP	0.41	0.36
3-BP	0.37	0.29
4-BP	0.35	0.30
2-IP	0.44	0.37
3-IP	0.39	0.35
4-IP	0.39	0.33

As can be seen from Table 1, the mobility increases from F<Cl<Br<I in the presence of both electrolytes. Because all of the halophenols came out after the neutral marker, they behave as if carrying a partial positive charge, probably through association with the electrolyte cation. In addition, the migration

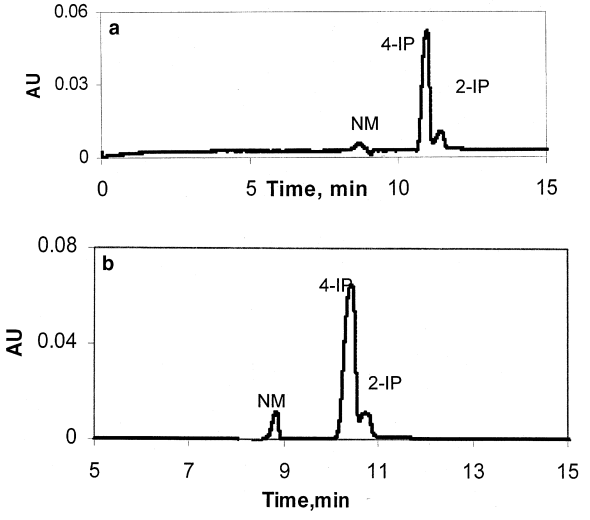

Fig. 1. (a) CE separation of 2-IP and 4-IP in 200 m*M* [NEt_4][BF_4] solution. (b) CE separation of 2-IP and 4-IP in 150 m*M* [emim][BF_4] solution.

Table 2
Average mobilities ($n=3$) for some analytes in 200 m*M* $[NEt_4][BF_4]$

Analyte	Mobility alone -(10^{-4} cm^2 V^{-1} s^{-1})	Mobility for analyte pairs-(10^{-4} cm^2 V^{-1} s^{-1})
2-BP	0.41 + 0.01	0.40 + 0.01
4-BP	0.35 + 0.01	0.35 + 0.01
2-IP	0.44 + 0.01	0.44 + 0.01
3-IP	0.39 + 0.01	0.39 + 0.01

order indicates that the larger the hydrophobic surface of the analyte, the higher the affinity.

Another interesting feature is that the site of the substituent also affects the mobility. Using anodic detection, positively charged analytes migrate after neutral marker but are eventually carried towards detector by the electroosmotic flow. Thus, the isomer that elutes later has higher affinity for the cathodically migrating cations than the earlier migrating isomer. The same trend was observed for halophenols in both the $[emim][BF_4]$ and $[NEt_4][BF_4]$ experiments.

In the case of $[NEt_4][BF_4]$, the mobilities of analytes when run alone or in pairs with their isomers (Table 2), exhibited no difference. However, in the course of determining the electrophoretic mobilities for the mixtures of phenols, discrepancies in electrophoretic mobilities became apparent, when using $[emim][BF_4]$. Injections of single component samples yielded good migration time reproducibility but compound mixtures (Table 3) did not, suggesting possible higher association occurring in solution. In the mixtures, the analytes came out faster than individual analytes suggesting either weaker association with the cation or possible higher order association involving more than one phenolic molecule and imidazolium. Separation efficiency also degraded in the mixtures relative to individual electrophoretic runs (e.g. $N_{\text{two component}}$ ~3900 vs. $N_{\text{one component}}$ ~4400).

Table 3
Average mobilities ($n=3$) for selected analytes in 150 m*M* $[emim][BF_4]$ solution

Analyte	Mobility alone -(10^{-4} cm^2 V^{-1} s^{-1})	Mobility for mixture, -(10^{-4} cm^2 V^{-1} s^{-1})
2-CP	0.33 + 0.01	0.26 + 0.01
4-CP	0.29 + 0.01	0.23 + 0.01
2-BP	0.36 + 0.01	0.33 + 0.01
4-BP	0.30 + 0.02	0.29 + 0.00
2-IP	0.37 + 0.02	0.32 + 0.01
4-IP	0.33 + 0.01	0.28 + 0.01

Compounds capable of forming hydrogen bonds, such as the phenols, may self-associate or associate with other hydrogen bonding species [26,27]. However, the data suggests that the imidazolium cation may play a role in promoting association not observed with the tetraalkylammonium cation. Nuclear magnetic resonance studies were conducted to explore further these results.

3.2. NMR results

Nuclear magnetic resonance has been used to study inter- and intramolecular interactions in the solution because it is possible to distinguish hydrogen bonding interactions from stacking interactions [28,29].

Four electrolyte concentrations were explored, 1, 50, 100, and 150 m*M* of either $[emim][BF_4]$ and $[NEt_4][BF_4]$. The iodophenols were chosen for this investigation because they exhibited the highest affinity for both electrolytes and 2-IP was well separated from 4-IP. Their structures are presented in Fig. 2.

The NMR spectrum containing $[emim][BF_4]$ and both phenols is presented in Fig. 3. The NMR spectra of 2-IP consists of 4 non-equivalent protons, a doublet at 7.57 ppm (H3, $J=7.9$ Hz), a triplet at 7.09 ppm (H5, $J=8.0$ Hz), a doublet at 6.52 ppm (H6, $J=8.1$ Hz) and a triplet at 6.75 ppm (H4, $J=8.0$ Hz). For 4-IP, there are two doublets in the spectra: H2 and H6 at 6.51 ppm ($J=8.7$ Hz) and H3 and H5 at 7.37 ppm ($J=8.7$ Hz).

Experiments done with $[NEt_4][BF_4]$ revealed that

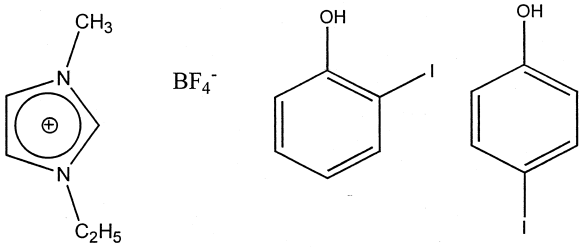

Fig. 2. Structures of $[emim][BF_4]$ and iodophenols.

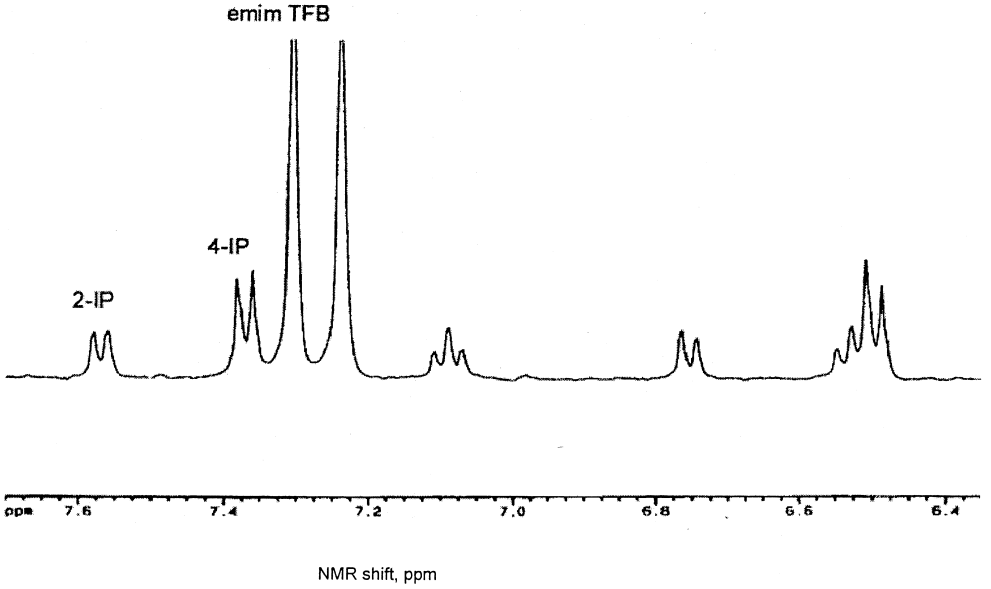

Fig. 3. ^{1}H NMR spectra of 150 m*M* [emim][BF_4] and 8.5 m*M* 2-IP and 4-IP solution.

there was no significant shift observed for any of the protons of the cation. Experiments done with [emim][BF_4] and iodophenols revealed that while the protons of ethyl and methyl group of the imidazolium cation were not affected by the presence of phenol, the phenolic and imidazolium ring protons did shift. Thus, the interaction appeared to be between the imidazolium and the phenyl rings. The imidazolium H2 proton was not seen in the spectra because it exchanges easily in the presence of $^{2}H_2O$ [30].

All changes in the chemical shifts of the phenolic protons were approximately the same with respect to the change in the concentration of either electrolyte or phenolic concentration. This implies that the phenol did not assume any specific orientation with respect to the imidazolium ring. Therefore, the most downfield peaks were chosen to assess the environmentally induced changes in phenolic chemical shifts. The chemical shift of H5 of imidazolium (singlet at 7.30 ppm) was chosen to assess the change in local environment when changing electrolyte or phenol concentration.

A mixed titration experiment was conducted in which the first and second addition contained the phenol of interest while the third and the fourth additions contained a related phenol and the spectrum was recorded after each addition. In the first addition, 20 μl of 0.13 *M* 2-IP were added to the electrolyte. For the second addition, 20 μl more of 2-IP were added. For the third addition, 20 μl of 0.13 *M* 4-IP were added to solution. The final addition consisted of 20 μl more of 4-IP solution added. The initial 2-IP concentration was 4.7 m*M*, and with successive additions resulting in concentrations 9.1, 8.8, and 8.5 m*M* 2-IP, respectively. The same protocol was repeated for all concentrations of both electrolytes. The data for the shift of the selected 2-IP peak is plotted in Fig. 6, where chemical shifts of the first downfield peak of 2-IP (H3) are plotted for four different concentrations of [emim][BF_4] through the addition of iodophenols.

3.2.1. NMR results for [emim][BF_4]

Two types of perturbations in Fig. 4 may be seen: one emanating from the addition of the phenol, the other emanating from the different electrolyte concentrations. Perturbations in the NMR spectrum produced by the first addition of 2-IP supports self-association of 2-IP while the addition of the 4-IP supports mixed association between the phenols. As can be seen from Fig. 4, independent of electrolyte concentration, addition of 2-IP to 2-IP causes the proton resonance to shift upfield indicating shielding,

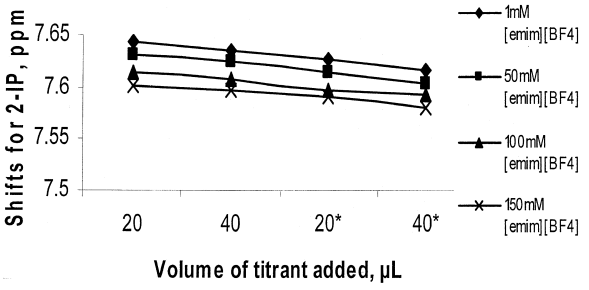

Fig. 4. Shift of selected 2-IP peak depending on concentration of [emim][BF_4], 2-IP, and 4-IP. * First two additions are 2-IP, the last two additions are 4-IP.

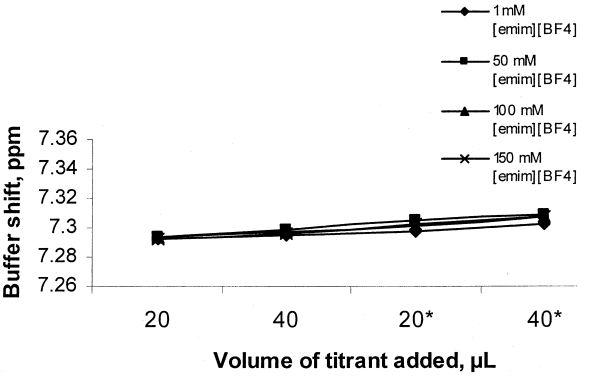

Fig. 5. Shift of selected [emim][BF_4] peak depending on concentration of 2-IP and 4-IP. * First two additions are 2-IP, the last two additions are 4-IP.

possibly through π–π stacking. Self-association of phenol and substituted phenol in non-aqueous solutions has been reported [31–33]. However, this has been ascribed to hydrogen bonding. While hydrogen bonding may seem likely because of the OH groups on the phenol, hydrogen bonding would produce a downfield shift [34]. Thus, π–π stacking, enhanced by nonspecific hydrophobic interaction, seems to be the preferred interaction in this case. The chemical shift reflects the relative populations in the free and complexed states of 2-IP. A shift in the same direction and magnitude occurs when 4-IP is added indicating a similar interaction. The complimentary experiments starting with addition of 4-IP and then 2-IP produced similar data.

A definite [emim][BF_4] electrolyte concentration effect was also observed. Increased concentration of [emim][BF_4] electrolyte also led to increased shielding with phenolic proton peaks shifted upfield. A concentration dependent chemical shift indicates fast exchange, which is consistent with weak binding reported by Yanes et al. [12] between catechin and [emim][BF_4].

The data for the H5 proton on the imidazolium ring obtained using [emim][BF_4] during the same experiments is shown in Fig. 5. The magnitude of the shift is much smaller than those observed for the phenolic protons and the differences among data points may be experimental error. The changes in chemical shift for the imidazolium ion are dependent on several competing factors. Decreasing imidazolium concentration in acetone has been shown to elicit an upfield shift due to hydrogen bonding [35]. However, the strong hydrogen bonding ability of water loosens the imidazolium cation–anion pair association and there is only a negligible concentration effect [36]. However, π–π stacking with the phenols should produce an upfield shift. Thus, the impact of changes in phenol concentration on the imidazolium proton chemical shift is negligible.

3.2.2. NMR results for [NEt_4][BF_4]

The data for the same experiments with [NEt_4][BF_4] is represented in Fig. 6, where the chemical shift of the selected 2-IP peak is plotted versus addition of phenols at four different con-

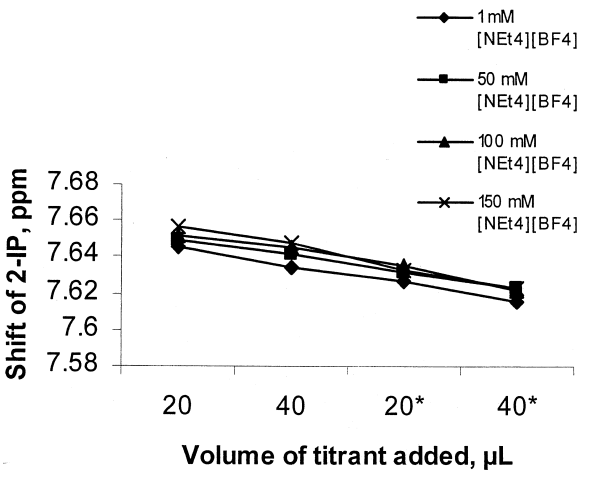

Fig. 6. Shift of selected 2-IP peak depending on concentration of [NEt_4][BF_4] and 2-IP and 4-IP. * First two additions are 2-IP, the last two additions are 4-IP.

centrations of electrolyte. When changing the concentration of phenols, the overall change in the chemical shift of the 2-IP peak is about the same as in the case of [emim][BF_4], indicating that phenols also self-associate in the presence of [NEt_4][BF_4]. The difference in chemical shifts at different concentrations of electrolyte is less than in the case of [emim][BF_4], indicating that phenolic self-association is fairly insensitive to [NEt_4][BF_4] concentration. The chemical shift of 2-IP protons moves downfield with increased electrolyte concentration indicating that the interaction between phenols and the cation is different from the interaction between phenols and the imidazolium cation.

The difference between the two electrolyte solutions the best may be ascertained from Fig. 7, where the chemical shift of the 2-IP peak, at concentration 4.7 m*M*, is plotted versus different concentrations of [emim][BF_4] and [NEt_4][BF_4]. The interaction between [emim][BF_4] and the iodophenol appears to be stronger than the interaction between [NEt_4][BF_4] and the iodophenol. If the observed shift of phenolic protons in [emim][BF_4] arose solely from methanol addition, the same difference in shifts should be observed in the case of [NEt_4][BF_4]. However, the differences in chemical shifts between the two electrolyte systems are clearly the result of fundamental differences in the cations of the electrolytes.

Upfield shifts can be interpreted in terms of molecular association by vertical stacking of rings or π–π stacking. The imidazolium cation promotes the base stacking of the phenols because there is no upfield shift observed in case of [NEt_4][BF_4]. It is expected that the same type of interaction takes place between [emim][BF_4] and other halogenated phenols.

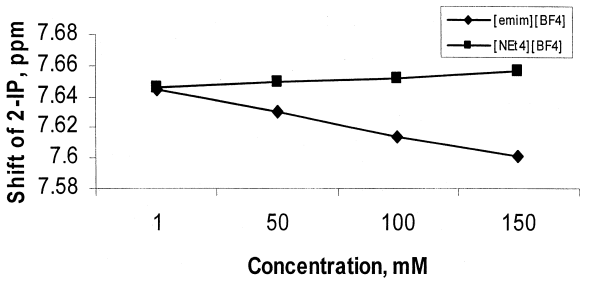

Fig. 7. Shift of selected 2-IP peak depending on concentration of [emim][BF_4] and [NEt_4][BF_4].

Fluorine NMR experiments were also performed in both electrolytes to assess the effect of concentration of phenols on the chemical shift of the anion. In the fluorine spectra, two resonance peaks are observed due to a boron isotope effect. NMR isotope shifts arise from averaging bond vibrations, which are mass dependent. Magnitudes of isotope effects on chemical shifts depend on the range of chemical shifts of the observed nucleus. The lighter atom has greater amplitude than the heavier, altering the shielding of other nuclei in the molecule (secondary isotope effect) [37]. Substitutions with heavy isotopes shift the NMR signal of a nearby nucleus toward lower frequencies, which can be seen in fluorine NMR spectra in Fig. 8. The smaller peak in the spectrum arises from fluorine attached to B^{10}, which is ~20% isotopic abundance. The selected peak for observing the chemical shifts is shown in Fig. 8.

Fig. 9 represents the changes in fluorine chemical shift, which occurs by adding phenols to the 150 m*M* [emim][BF_4] solution or 150 m*M* [NEt_4][BF_4] solution, using the same protocol as in the case of proton NMR. Identical results were obtained with either electrolyte. Thus, the tetrafluoroborate role is identical in both systems and observed differences (e.g. CE, NMR) arise from differences in the interactions with the cation. The fluorine is more sensitive to changes of surrounding environment than the protons; thus, the changes in fluorine's chemical shift cannot be directly compared with the proton shifts. However, as can be seen, the concentration of the phenols does affect the fluorine shift, indicating that there is some interaction between anion and the phenols as well.

NMR experiments support possible association between the cations of the electrolytes and the halophenols. NMR results also support the role of the imidazolium cation in promoting association between the phenols, which may explain some of the CE reproducibility issues observed using this system.

4. Conclusions

CE results indicate that the interactions between

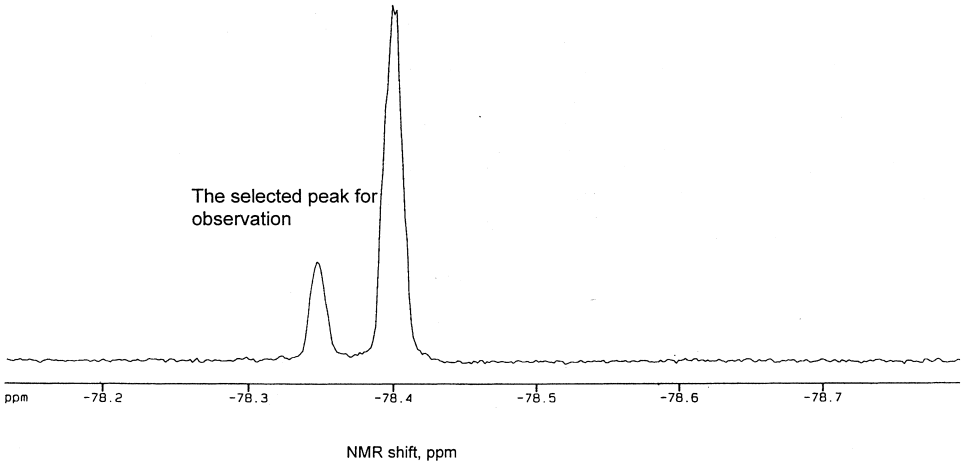

Fig. 8. ^{19}F NMR spectra of 150 m*M* [emim][BF_4].

halophenols and cations of ionic liquid or tetra-alkylammonium salt are similar to those reported previously for polyphenols. The halophenols behave as though carrying a positive charge through association with the cation of the electrolyte. Separation was achieved for some bromo- and iodophenols using both electrolytes, and partial separation was achieved for some chlorophenols. The electrophoretic mobility of the fluorophenols was too close to get separation in any case. The affinity towards the cations depends on the size of the halogen as well as the site of the substituents. Iodophenols have the largest negative electrophoretic mobility and highest affinity for the cations. In all cases, 2-substituted halophenols came out after the 4-substituted halophenols.

NMR studies suggest that [emim][BF_4] promotes association between the phenols. NMR studies show

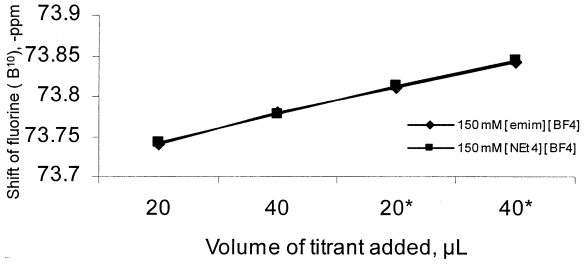

Fig. 9. Shift of selected fluorine peak depending on the concentration of 2-IP and 4-IP in 150 m*M* [emim][BF_4] and 150 m*M* [NEt_4][BF_4]. * First two additions are 2-IP, the last two additions are 4-IP.

that the interaction mechanism for phenols involves $\pi-\pi$ stacking. In the case of interactions between imidazolium and phenols, the mechanism is not clear but suggests that imidazolium also promotes phenol stacking.

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