Ionic liquids as background electrolyte additives and coating materials in capillary electrophoresis

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Abstract. Now that many scientific investigations focus on ionic liquids (IL) to establish their potential in different chemical processes, their application for the separation of various classes of compounds in capillary electrophoresis has also been recognized. ILs have been used as background electrolytes in aqueous and non-aqueous capillary electrophoresis for the separation of a number of different analyte types providing both control of the electroosmotic flow and the charging of analytes. Besides this ILs are used as micelle-forming compounds and capillary wall modifiers, as well as separation media additives in NACE for contactless conductivity detection.

Key words: capillary electrophoresis, ionic liquids, non-aqueous capillary electrophoresis.

INTRODUCTION

Despite the pioneering work of Walden [1] already in 1914, room temperature molten salts or ionic liquids (ILs) have only become popular during the last decade. ILs have often been more appropriately called 'designer solvents' to indicate the large structural variability of either the cation or the anion of the salt, which accounts for their broad application area. Early applications of ILs for analytical separations have been described in several reviews [2–5]. There are a few studies where ILs have been used in thin-layer chromatography as eluent additives [6]. ILs serve mainly as electrolyte additives in capillary electrophoresis (CE) and in mobile phases for high-performance liquid chromatography (HPLC). They dissolve well in organic solvents, thus broadening the relatively limited list of suitable buffer additives for non-aqueous capillary electrophoresis (NACE). Organic solvents are of interest in capillary electro-separation because

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they extend the range of the application of CE techniques to more hydrophobic species, addressing one of the main limitations of this method.

Electromigration methods compose a family of analytical separation methods based on differences in the mobilities of charged analytes in the electric field. In this paper we discuss mainly such electromigration methods that are performed in thin capillaries with i.d. less than 0.1 mm. These methods are commonly known as capillary electrophoretic methods where the most important modes are capillary zone electrophoresis (CZE), micellar electrokinetic capillary chromatography (MECC), capillary gel electrophoresis (CGE), and capillary electrochromatography (CEC). Differences in the mobility of the analytes due to their average charge, size, and shape and the properties of the electrolyte solution used form the basis of a valuable separation method in chemistry.

IONIC LIQUIDS AS BACKGROUND ELECTROLYTE ADDITIVES IN NON-AQUEOUS MEDIA

Interest in ILs used as separation media in capillary electromigration methods is due to the fact that they can provide an alternative separation mechanism to two widely implemented mechanisms that base either on the charge to mass ratio or hydrophobicity of analytes.

Among background electrolyte additives, dialkylimidazolium-based ILs are the most widely used. These liquid organic salts were for the first time proposed for the non-aqueous background electrolyte system by Vaher et al. [7–9]. In these studies ILs were used as an ingredient to form the background electrolyte. The miscibility of these ILs with acetonitrile makes them easy to use for the adjustment of analyte mobility and for the separation in NACE. Various 1-butyl-3-methylimidazolium $\{[C_4MIm][X]\}$ based ILs where $X=PF_6^-$, CH_3COO^-, CF_3COO^-, $(CF_3SO_2)_2N^-$, $CF_3(CF_2)_2COO^-$ have been used for the separation of water insoluble dyes [7], phenols, aromatic acids [8], and polyphenols [10] in acetonitrile (ACN). In [8] it was demonstrated that imidazolium based ILs do not change the direction of the electroosmotic flow (EOF) in the capillary in various organic solvents. Studies [7–10] revealed that the nature of the anionic part of ILs affects slightly the electrophoretic mobility and the IL concentration influences the general electrophoretic mobility of the separation media. The separation of dyes was achieved because they dissociate in the presence of ILs (as well as in the presence of some phenolic compounds) or associate with the IL anion via a process known as heteroconjugation [11]. In CE the ACN is the main solvent where heteroconjugation based separations can be observed and measured [11]. However, usually the picture is more complicated; for example Miller et al. showed that by the separation of acidic solutes combination of heteroconjugation and deprotonation can take place [12].

In the case of methanol as the solvent, alkylimidazolium salts can assist in separating metal cations [13]. The separation of Na^+, K^+, Ca^{2+}, and Mg^{2+} ions in

mineral water was achieved by using 20 mM of 1-butyl-3-methylimidazolium heptafluorobutanoate ($[C_4MIm][CF_3(CF_2)_2COO]$) in methanol with indirect UV detection. Under these conditions alkali and alkaline earth metal cations are well separated without using any of the complexing agents.

One of the disadvantages of imidazolium based electrolytes is their non-transparency for UV light in the region 190–245 nm. Borissova et al. [14] demonstrated that contactless conductivity detection may be applied in the monitoring of the separation process in non-aqueous separation media, allowing the use of UV light absorption in imidazolium-based electrolyte additives.

As illustrated in Fig. 1, the addition of 7 mM of 1-ethyl-3-methylimidazolium ethylsulphate ($[C_2MIm][EtSO_4]$) to ACN results in perfect separation of 1-butyl-3-methylimidazolium methylsulphate ($[C_4MIm][MeSO_4]$), 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIm][PF_6]$), and 1-decyl-3-methylimidazolium bis(pentafluoroethansulphonyl)imide ($[C_{10}MIm][Pf_2N]$). In another experiment (Fig. 2), the addition of 20 mM of 1-butyl-3-methylimidazolium trifluoroacetate ($[C_4MIm][FAcO]$) to ACN led to the total resolving of five different cations of ILs. The separation may occur due to the interaction of analytes with IL ions in the separation medium. Cations of analytes with different lengths of alkyl side-chains interact differently with the background electrolyte (BGE) additive.
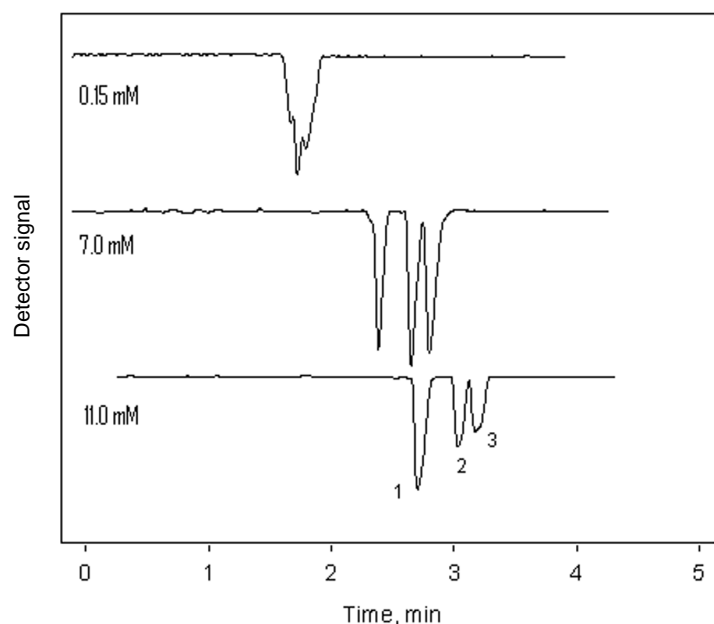

Fig. 1. Separation of ionic liquids in acetonitrile using $[C_2MIm]$ $[EtSO_4]$ as additive. 1 – $[C_4MIm]$ $[MeSO_4]$, 2 – $[C_8MIm]$ $[PF_6]$, 3 – $[C_{10}MIm]$ $[Pf_2N]$. Applied voltage 18 kV; injection hydrodynamically h = 15 cm for 5 s.
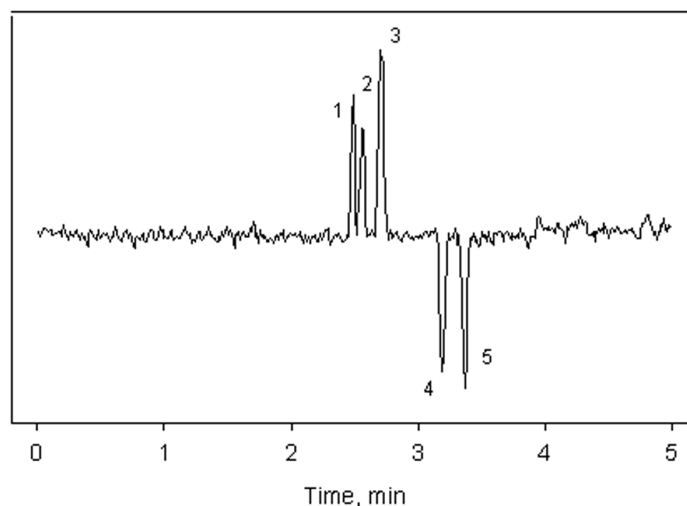
Fig. 2. Separation of ionic liquids in acetonitrile modified with [C$_4$MIm] [FAcO] (20 mM) additive. 1 – [C$_1$MIm] [MeSO$_4$], 2 – [C$_2$MIm] [EtSO$_4$], 3 – [C$_4$Mpyr][dca], 4 – [C$_8$MIm] [PF$_6$], 5 – [C$_{10}$MIm][Pf$_2$N]. Applied voltage 18 kV; injection hydrodynamically h = 15 cm for 5 s.

An interesting approach is the use of some physical event as an independent marker of the EOF instead of chemical compounds, and short thermal pulses appear to be one possible solution for that [15]. The so-called thermal mark makes it possible to observe whether there are changes in the EOF during the separation process. Our recent study demonstrates that (Fig. 3) the thermal mark can be used in organic solvents where ILs are used as BGEs and comparison of the EOF value of a chemical marker with that of the thermal mark showed them to be almost identical.

The separation mechanism in CE with IL ingredients has recently been studied very thoroughly with the help of powerful mathematical tools such as experimental design and linear solvation free energy formalism. The aim of a study by François et al. [16] was to elucidate the influence of the IL concentration on the electrophoretic behaviour of four arylpropionic acids and to identify the interaction between the analytes and the IL cation. The presence of 1-butyl-3-methylimidazolium bis(tetrafluoromethansulphonyl)imide [C$_4$MIm][Tf$_2$N] in ACN/alcohol BGEs was investigated in that work. The influence of the IL concentration on the mobility of the EOF, the nature and the proportion of the organic solvents, and the concentration of the ionic components of the BGE were studied by a four-factor D-optimal experimental design. It enabled to provide a deeper insight into analyte interaction with IL cation present both in BGE solution and adsorbed onto the capillary wall. It was found that the electrophoretic mobilities of analytes pass through a maximum for a given IL concentration around 7 mM. Such behaviour was not anticipated from a simple possible interaction between anionic analytes (profens) and the IL cation present in BGE
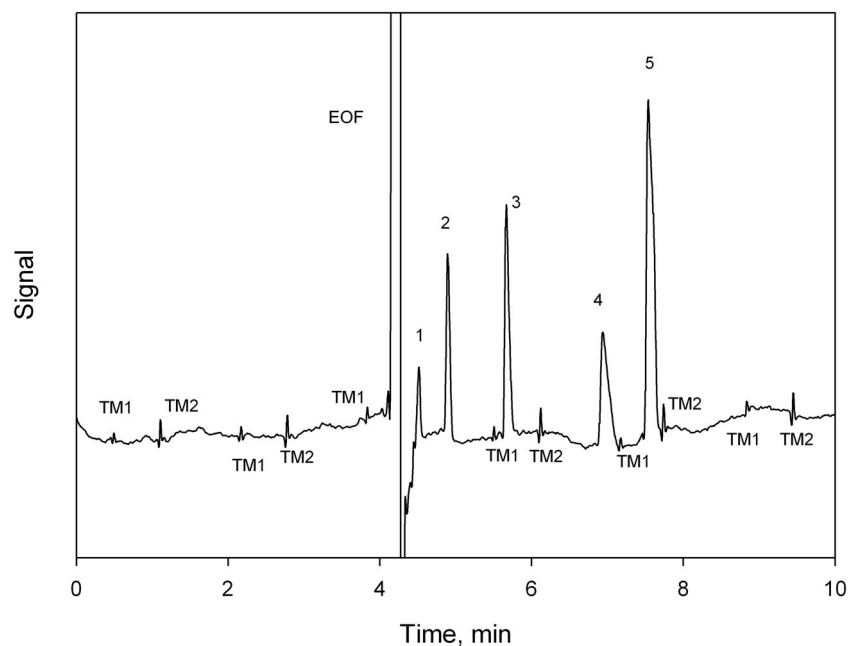
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Fig. 3. Monitoring of EOF stability during the separation of derivatives of benzoic acid using a thermal mark. TM1 – first thermal mark, TM2 – second thermal mark; 1 – aminobenzoic acid, 2 – benzoic acid, 3 – 3,5-dihydroxybenzoic acid, 4 – salicylic acid, 5 – 3,5-dinitrobenzoic acid. Background electrolyte: 5 mM [C$_4$MIm][FAcO] in acetonitrile.

as it would have led to a monotonous decrease in the electrophoretic mobilities of profen. Instead, it may rather be explained by competitive interactions between profen and the IL cation adsorbed onto the capillary wall or into the free IL cation present in the BGE.

Attempts to separate cations of ILs in pure ACN have failed. When the sample consists of toluene (as a neutral marker), and traces of IL, then the IL migrates slower than the neutral marker. This suggests that some form of retention against a neutral marker of the IL may occur in pure ACN. This observation may be explained by the adsorption–desorption of the IL on the capillary wall. The IL may migrate in this medium in the form of ion pairs whose cations interact with the capillary surface. The retention of ILs against the neutral marker disappears when their concentrations in the sample are increased. The EOF velocity follows a decreasing trend with the increasing additive concentration. The change in the migration of the analytes with the change of the BGE concentration follows a trend similar to the conductivity of the electrophoretic medium described in [17]. The addition of IL to ACN increases the conductivity of BGE. The conductivity then reaches the maximum and relatively slowly decreases as the IL concentration in the separation medium increases.

To design a relevant separation protocol for the given analytes in CE, it is necessary to develop a method by choosing suitable ILs or mixtures of ILs and

organic solvents with exactly the right properties for chromatography and electrophoresis, especially in terms of viscosity, conductivity, and absorbance of UV light. Determination these properties on ILs can be rather time-consuming and expensive, requiring individual tests for each property and large sample sizes (several millilitres). To address this issue, a team of chemists led by P. Gareil developed a single test for measuring these properties by taking advantage of CE [16]. In their test a CE capillary was filled with an IL and then its UV absorbance was measured using a standard diode array detector (DAD). To measure the viscosity, they introduced a plug of the flow marker into the tube and then injected the IL until the marker reached the end of the tube and was plotted by the DAD. Using the Hagen-Poiseuille law, the time it takes the flow marker to reach the detector can be used to calculate the viscosity. The conductivity was calculated by simply applying a voltage across the tube and measuring the electrical current after the flow marker had been pushed out.

In recent years ILs have been applied as matrices for matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) [18], thus expanding the use of MALDI. In [13] the suitability of alkylammonium and alkylimidazolium salts of α-cyano-4-hydroxycinnamic acid was investigated as a MALDI matrix and at the same time as the additive of BGE. The alkylammonium salt produced better separation of phenolic compounds than the alkylimidazolium salt. The investigation suggests that it is possible to synthesize ILs suitable for electrophoretic analysis as well as for on-line MALDI-MS analysis.

IONIC LIQUIDS AS BACKGROUND ELECTROLYTE ADDITIVES IN AQUEOUS MEDIA

Yanes and co-workers [19] demonstrated an application of IL for aqueous CE for the separation of phenolic compounds found in grape seed extracts. By using [C_2MIm] and [C_4MIm] ILs as additives for the running electrolyte, a simple and reproducible electrophoretic method for the separation of polyphenols was developed. In this case the interactions occurred through π–π interactions between phenolic compounds and the IL cations in water. The imidazolium ions present in the CE BGE cover the capillary walls, generating an anodic EOF. The neutral polyphenols (pKa = 9.5–10.5) can associate with either the imidazolium cation coating on the capillary wall or with the free cations in the bulk solution and thus be separated (Fig. 4). Experiments show that association of polyphenols with the free imidazolium ion seems to dominate.

The following research supported the previous findings by Yanes et al. [19]. It is well established for now that with the presence of ILs in the running buffer the imidazolium ions adsorb on the capillary wall. A common problem in CE separation of basic proteins is the negatively charged surface of the capillary, which electrostatically attracts the positively charged sites of proteins. The ILs on the surface are blocking these sites and allow less interaction of analytes with the capillary surface. Jiang et al. [20] added imidazolium-based ILs into the running
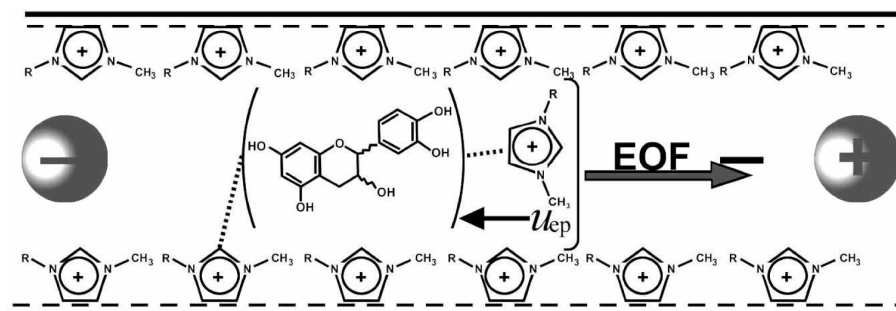
Fig. 4. Mechanism of the separation of polyphenols using 1-alkyl-3-methylimidazolium-based ionic liquids [19].

electrolyte to dynamically cover the capillary for successful CE separation of basic proteins such as lysozyme, cytochrome *c*, trypsinigen, and α-chymotrypsin A.

In another application Cabovska et al. [21] investigated the CE behaviour of monohalogenated phenols in the presence of $[C_2MIm][BF_4]$ and compared the results with those obtained with tetraethylammonium tetrafluoroborate $[Et_4N][BF_4]$ electrolytes. These results indicate that the interactions between halophenols and cations of ILs or tetraalkylammonium 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.

ILs were tested as additives to the phosphate–acetate buffer for the separation of chlorophenoxy and benzoic herbicide acids [22]. Again it was found that in the 40 mM phosphate–acetate BGE containing 10% ACN and having pH 4.5, the addition of 10 mM of 1-butyl-3-methylimidazolium could reverse EOF. The shoulder-merged peaks of two herbicide acids were successfully resolved by the addition of IL. Apart from this, the results showed that different IL cations have different influences on the migration behaviour of some of the analytes, while IL anions do not introduce any obvious difference to the separation.

The ILs as the minor additive of borate buffer are very widely applied to separate different classes of analytes including chiral compounds [23–27].

ANALYTICAL APPLICATION OF IONIC LIQUIDS AS A MICELLE-FORMING SURFACTANT

The amphiphilic character of ILs with long alkyl chains induces the behaviour similar to that exhibited by cationic surfactants – in appropriate conditions they start to form aggregates. This makes them attractive for application as a micelle-forming component in MECC separations. However, only a few examples of the analytical utility of long-chain ILs as self-assembled compounds [28] or as buffer additives [29] for MECC separations have been presented.

Table 1. Values of critical micelle concentration (mM) measured by the spectrophotometric method at 298 K

	[C_{12}tma]Cl	[C_{12}MIm]Cl	[C_{14}tma]Cl	[C_{14}MIm]Cl
Water	21	12.5	5	3.5
25 mM phosphate buffer	13.5	5	2	2.5

Borissova et al. carried out an investigation for the determination of the critical micelle concentration (CMC) of long-chain imidazolium based ILs and with the respective chain length of alkyltriammonium salts in water and 20 mM phosphate buffer. The CMCs were measured by a method based on changes in the optical properties of surfactant solutions using the UV–Vis spectroscopic technique [30]. Table 1 gives the measured CMC values of the surfactants used. The ability of alkylimidazolium ILs to act as micelle-forming surfactants not only in pure water but also in the traditional electrophoretic separation buffer was proven by the separation of resorcinol and three methylresorcinol isomers and some hydrophobic benzene-type analytes. All these analytes remain neutral at the given pH of the separation buffer. So, their separation involves the separation principles based on the analytes partitioning between a micellar stationary phase and a bulk electrolyte. At IL concentrations below CMC almost no separation of analytes was observed. Nevertheless in some cases the introduction of an additional separation force via the combination of analyte–micelle and analyte–IL cation interactions was observed.

IONIC LIQUIDS AS CAPILLARY WALL MODIFIERS

In order to reverse the EOF direction in the silica capillary, ILs can be covalently bound also to the internal surface of the capillary and a permanent coating will be obtained. This approach was applied to separate positively charged drugs [31], DNA [32], and ammonium and metal ions by CE–potential gradient detection using ILs as BGE and covalently coated capillary [33, 34]. Experiments showed that the covalently ILs-coated capillary could be used for at least 80 h with relatively stable EOF. Another advantage of covalent coating of the capillary inner surface with ILs is that the system becomes compatible with MS; whereas dynamic coating is not compatible with MS because ILs are non-volatile compounds.

In order to reduce the interaction between the analytes and the capillary wall, as well as to modify the magnitude and direction of EOF, imidazolium-based IL analogues were permanently bounded to the capillary wall in two different ways – heterogeneously and homogeneously [35]. Both types of wall coating resulted in the formation of the positive charge onto the capillary wall, but the density of the incorporated functional groups was higher in the case of homogeneous modification.
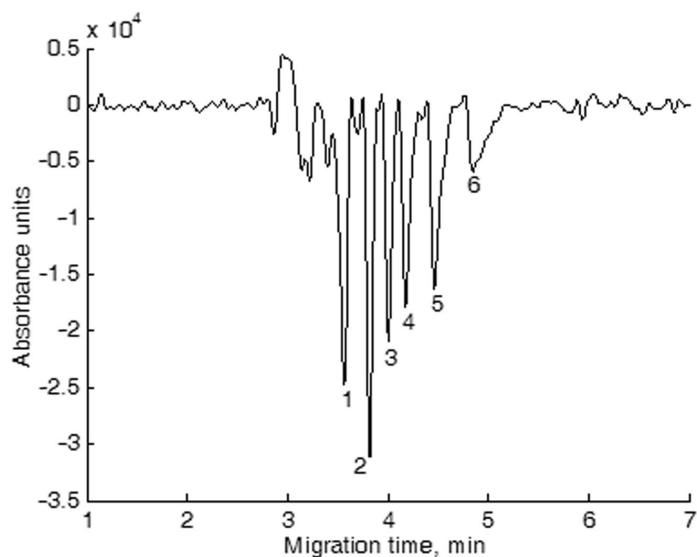
Fig. 5. Electropherogram of the separation of six alkylphosphonic acids/esters using a capillary coated with an ionic liquid analogue. Experimental conditions: 5 mM sorbic acid at pH 6.2; applied voltage – 25 kV; indirect UV detection at 254 nm. Analytes: 1 – methylphosphonic acid, 2 – ethyl methylphosphonate, 3 – ethylphosphonic acid, 4 – propylphosphonic acid, 5 – 1-butylphosphonic acid, 6 – pinacolyl methylphosphonate.

In a continuation of the study [36], the behaviour of permanent types of silica wall coatings at different pH values of the separation buffer was investigated. Thus, the imidazole-containing zwitterionic salt covalently attached to the silica capillary wall was characterized by the cathodic electroosmotic flow and by an almost constant velocity in the pH range of 4 to 7. The EOF in the capillary coated with an IL analogue was found to be anodic and strongly dependent on the pH of the separation buffer.

The separation performance of the capillary coated with an IL analogue in an aqueous buffer was proved by the separation of six alkylphosphonic acids and their esters (Fig. 5). The separation was accomplished in less than 6 min using a simple separation buffer (5 mM sorbic acid) without incorporation of any BGE additives. The effectiveness of the coating in non-aqueous media was investigated by successful separation of natural phenolic compounds [35].

CONCLUSIONS

It follows from the discussion above that the chemistry of ILs as additives in the electrolyte for CE is rich and promising. Many questions remain still unanswered and the area of further research is extensive. IL applications have demonstrated the usefulness of IL for the separation of complicated analytes such as positional isomers and for charging neutral hydrophobic analytes in NACE.

Another important feature of ILs is that they can effectively reduce or reverse the EOF in the capillary. This process is more pronounced if an IL is covalently attached to the capillary wall.

With the development of new ILs of suitable structure–property relationships they could assume a prominent role in the separation science.

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Ioonsed vedelikud taustelektrolüütide ja pinnakattematerjalina kapillaarelektroforeesis

Merike Vaher, Maria Borissova, Mihkel Koel ja Mihkel Kaljurand

Tänapäeval on paljud uuringud koondunud ioonsetele vedelikele, määramaks nende potentsiaali erinevates keemilistes protsessides. Tunnustust on leidnud nende kasutamine kapillaarelektroforeesis erinevate ainete lahutamiseks. Ioonseid vedelikke on kasutatud taustelektrolüüdi komponendina kapillaarelektroforeesis nii vesi- kui ka mittevesikeskkonnas, kusjuures nad mõjutavad nii elektroosmootset voogu kui ka analüütide laengute omastamist. Lisaks neile juba levinud rakendustele kasutatakse ioonseid vedelikke lahutuskeskkonnas mitselle moodustava ainena ja kapillaari seina modifitseerijana, samuti ka uute detekteerimissüsteemide jaoks.