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Imidazolium ionic liquids as dynamic and covalent modifiers of electrophoretic systems for determination of catecholamines

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ABSTRACT

The subject of this study is comparison of imidazolium based dynamic and covalent coatings of the quartz capillary wall on the example of catecholamines determination. A way of synthesis of covalent coatings was proposed. For the first time different type of *on-line* sample preconcentration techniques (*field-amplified sample stacking (FASS), head-column field amplified sample stacking (HC FASS), electrostacking, sweeping*) were performed for catecholamines determination in N-alkylsubstituted imidazolium coated capillary.

It was found that long chain imidazolium ionic liquids (C_{12}MImCl and C_{16}MImCl) in background electrolyte content create a dynamic coating of the quartz capillary walls and generate anode electroosmotic flow. Same is true for covalent coatings based on N-alkylsubstituted imidazolium. Both coatings prevent sorption of catecholamines on the internal surface of the quartz capillary. As a result efficiency and peak symmetry are increased.

The maximum stacking efficiency factor (SEF) values for dynamic coatings were in range of 70–85, and limits of detection (LODs) were about 0.05 µg/ml under sweeping condition (micelle forming agent – C_{16}MImCl) when the electric conductivity of sample matrix was higher than electric conductivity of BGE. In case of covalent coating, the maximum SEF values were higher than 1000, and LODs were about 1–2 ng/ml under sweeping condition (micelle forming agent – sodium dodecyl sulphate) in combination with electrostacking.

1. Introduction

Capillary electrophoresis (CE) is a rapidly spreading, powerful and effective tool in the separation of charged or neutral compounds. Although capillary electrophoresis has the advantages of quickness and high efficiency when compared to high-performance liquid chromatography (HPLC), it has the shortcomings of low sensitivity, primarily due to combination of the short optical path length most commonly used for absorbance detection and the small sample volumes injected, and sorption of basic analytes on the quartz capillary walls. The performance of *on-line* preconcentration techniques is used to overcome the first limitation [1,2] and formation of the coating of the quartz capillary wall is the solution to the second problem [1]. In case of coatings, stability becomes an important factor, because it affects the reproducibility of the results.

The first type of coatings are dynamic that have become widespread due to the ease of creation. Dynamic coatings are formed because of physical adsorption of the modifier on the internal wall of the quartz capillary. There are many articles describing the usage of various compounds as dynamic modifiers [3] such as amines [4–8], polymers [9–12], surfactants and ionic liquids [13,14]. However, that coating has some disadvantages: it requires constant renewal and addition of the modifier to the background electrolyte (BGE). The covalent coatings – second type of coatings, do not require a modifier in BGE because of the formation through chemical bond, therefore it is stable. Initially, the modification was carried out using monomers, which during the reaction in vivo were transformed into polymers and were attached to the quartz capillary wall [15]. This approach is still used today [16–18].

The functionalization of covering is an interesting trend in CE [19,20]. Recently, major attention is brought toward ionic liquids (ILs) in analytical separation techniques. ILs have many properties making them excellent additives to background electrolytes (BGE) in capillary electrophoresis (CE). In CE they were used as pseudostationary phase (PSP) in micellar electrokinetic chromatography, as support coatings on

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Abbreviations: ILs, ionic liquids; C_{12}MImCl, 1-dodecyl-3-methylimidazolium chloride; C_{16}MImCl, 1-cetyl-3-methylimidazolium chloride; SDS, sodium dodecyl sulphate; EOF, electroosmotic flow; FASS, field amplified sample stacking; HC FASS, head-column field amplified sample stacking; SEF_h, stacking efficiency factor; t.p., theoretical plate number

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the quartz capillary wall and as a background electrolyte (BGE) in nonaqueous CE.

ILs are commonly known as organic salts with the melting points at or below 100 °C. In most cases, ILs are composed of an organic cation and an organic or inorganic anion. The possibility to easily vary the ions can be used for the synthesis of ionic liquids with required properties [21]. Previously imidazolium ILs were examined as reagents for covalent coating [22–26].

In [22] quartz capillary modified by ionic liquid was for the first time used for separation of DNA fragments. That capillary produced reversed electroosmotic flow (EOF) and provided reduction of analysis time compared to polyacrylamide coating. Another example of the usage of synthesized covalent coatings is the separation of metal ions [23,24]. The efficiency was increased due to the electrostatic repulsion of the metal ions from the positively charged walls of the capillary modified by IL based on imidazolium cation. The separation of manganese and lead was observed, which could not be performed on an unmodified capillary.

In [26] two types of coatings were created: analogue of the imidazole-based ionic liquid coating for separation of seven alkylphosphonic acids and coating based imidazole-contained zwitterionic salt for separation of inorganic anions. It was found that in modified capillary analysis time was longer without a significant loss of resolution compared to fused-silica capillary.

In [27] separation of neutral phenols was performed in ionic liquid modified capillary with using IL 1-butyl-3-methylimidazolium heptafluorobutanoate in background electrolyte content under non-aqueous capillary electrophoresis and results were compared with fused-silica capillary. It was found that in both capillaries the separation was performed with the same resolution during a short analysis time, but in the coated capillary analytes migrated in a reversed order because of the reversed EOF. Also separation of neutral phenols was described by the same scientific group [28] with usage of ionic liquid C_{14}MImCl as micelles forming agent. As a result, the separation of phenol and nitrobenzene was achieved, however, not on the baseline level due to the phenol peak tailing. Authors explained it through the different mechanism of separation: solute-micelle interaction for benzonitrile and nitrobenzene as neutral compounds in pH 7.0, in the case of phenol (pK_a 10) it involves both the solute-micelle and solute-cation interactions that lead to peak broadening.

Despite the large number of publications devoted to capillary coatings, the behavior of the biologically active substances on different coatings was not studied well enough, so in this work the effect of ionic liquids as an electrophoretic system modifier on separation of biogenic amines is investigated. Chosen analytes play an important role in diagnosis of endocrine and nervous systems diseases [29–33].

2. Materials and methods

2.1. Reagents and materials

Sodium hydroxide (analytical grade, "Khimreaktiv"); hydrochloric acid (high purity grade 4, "Reachem"); sodium dihydrogenphosphate dihydrate (cp grade "Reachem"); boric acid (cp grade "Reachem"); phosphoric acid (cp grade); 1-cetyl-3-methyl-imidazolium chloride (C_{16}MImCl, Acros Organics); 1-dodecyl-3-methylimidazolium chloride (C_{12}MImCl, Acros Organics), sodium dodecyl sulphate (SDS, Sigma); (-)-adrenaline (A) ("Sigma"); L-(-)-norepinephrine (NE) ("Aldrich"); DL-normetanephrine (NMN) ("Sigma"); dopamine (DA) ("Sigma"). Dichloromethane (> 99.7%, "J.T. Baker"), acetone (> 99.8%, "Merck"), N,N-dimethylformamide (DMF, > 99.9%, "J.T. Baker"), 1-bromobutane (99%, "ReagentPlus"), 1-bromooctane (99%, "ReagentPlus"), imidazole (> 99%, "Sigma-Aldrich"), (3-glycidyloxypropyl)trimethoxysilane ("Sigma"), 2,2-Diphenyl-1-picrylhydrazyl (DPPH) ("Sigma"), Na_2EDTA ("Sigma"), sodium carbonate (cp grade "Khimreaktiv"), ammonium acetate, glacial acetic acid ("Sigma-Aldrich"), Al_2O_3 powder (> 98%, "Sigma-Aldrich"), distilled deionized water.

2.2. Instrumentation

CE separations were performed using system of high efficiency capillary electrophoresis CAPEL'-105 M (Lumex, St. Petersburg, Russia) equipped with UV-spectrophotometric detector (wavelength range 190–360 nm); fused-silica capillaries with an external polyimide coating with the total capillary length 50 cm, effective length 60 cm, outside diameter 360 μm, and inner diameter 50 μm; an HI 2210–2216 pH-meter (Hanna); thermostat ("LOIP"), ultrasound bath "Elmasonic".

The processing of the results was carried out using the software "Elforan" and Microsoft Office Excel 2007.

Ultra-pure water from Millipore Milli-Q RG (Millipore, USA) was used for solutions preparation and dilution.

2.3. Experimental procedures

2.3.1. Preparation of stock and working solutions

The 1.0 mg/ml stock solutions of catecholamines (adrenaline, norepinephrine, dopamine, normetanephrine) were prepared in 0.1 M hydrochloric acid. The catecholamine stock solutions were stored at −16 °C until the electrophoretic analysis. The working solutions were prepared just before the experiments by a dilution of the stock solutions.

2.3.2. The synthesis of covalent coating of quartz capillary walls

2.3.2.1. Activation of the quartz capillary walls. Imidazolium-based ionic liquid was covalently coated onto the inner surface of fused-silica capillary by the following modified procedures (see Fig. 1) [34]: the

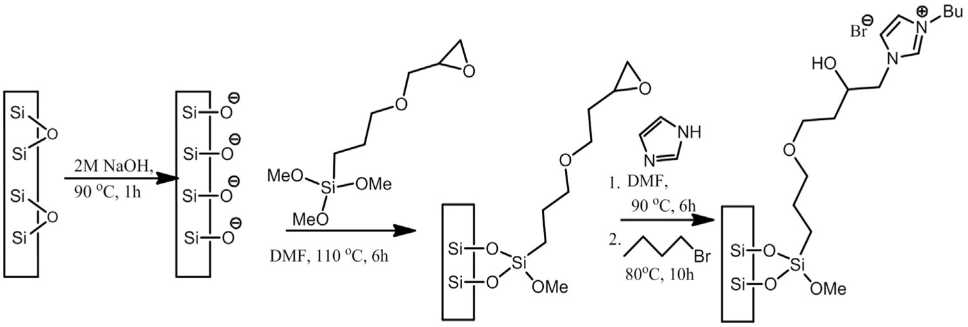

Fig. 1. The scheme of modified covalent coating synthesis based on substituted N-butylimidazolium [34].