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Quantitative aspects of electrolysis in electromembrane extractions of acidic and basic analytes

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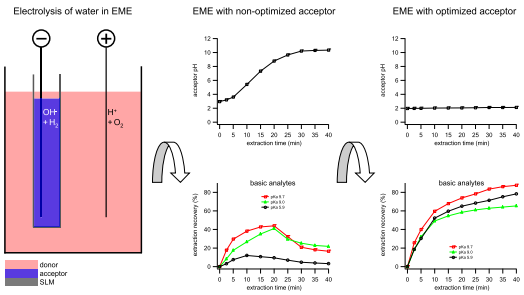
HIGHLIGHTS

- Effects of electrolysis on quantitative performance of EME were comprehensively evaluated.
- Changes of up to 8.5 pH units were observed in acceptor solutions during standard EMEs.
- Extraction recoveries of weak to medium strong acidic and basic analytes were thus seriously affected.
- Initial composition of acceptor solutions was shown crucial for proper EME performance.
- High concentrations of weak bases/acids were suggested as preferred acceptor solutions.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrolysis is omnipresent in all electrochemical processes including electromembrane extraction (EME). The effects of electrolysis on quantitative aspects of EME were comprehensively evaluated for a set of acidic (substituted phenols) and basic (basic drugs) analytes. EMEs were carried out across supported liquid membranes formed by 1-ethyl-2-nitrobenzene at standard EME conditions, i.e., acidic analytes were extracted from alkaline into alkaline solutions and basic analytes were extracted from acidic into acidic solutions. Electric potential applied across the EME systems was 50 V and extraction recoveries of analytes as well as pH values of donor and acceptor solutions were determined after each EME. It has been proven that electrolysis plays a more significant role than has ever been thought before in EME. Electrolytically produced H^+ and OH^- ions had a significant effect on pH values of acceptor solutions and variations of up to 8.5 pH units were obtained at standard EME conditions. pH values of donor solutions were affected only negligibly due to their significantly higher volumes. The observed variations in pH values of acceptor solutions had fatal consequences on quantitative EME results of weak and medium strong acidic/basic analytes. A direct relation was observed between the decrease in extraction recoveries of the analytes, their pK_a values and the acceptor solution pH values. Acceptor solutions consisting of high concentrations of weak bases or acids were thus proposed as suitable EME operational solutions since they efficiently eliminated the electrolytically induced pH variations, offered stable EME performances and were easily compatible with subsequent analytical methods.

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1. Introduction

Electromembrane extraction (EME) was introduced as a novel microextraction technique by Pedersen-Bjergaard and Rasmussen in 2006 [1]. The fundamental principle of EME relies on electrically induced transfer of charged species from one aqueous solution (donor) across a thin layer of a water immiscible solvent into second aqueous solution (acceptor). Involvement of the electric potential significantly increases extraction speed of EME compared to hollow fibre liquid phase microextraction, which is based on diffusive transfers of analytes [2], and an additional extraction selectivity is achieved in EME since only positively or negatively charged species can be transferred from donor into acceptor solution. Low cost, instrumental simplicity, minimum environmental impact and compatibility of acceptor solutions with all major analytical techniques are other advantages of EME. Several theoretical papers were published in the past describing possible models for the EME transfer of charged species [3–7] as well as numerous articles reviewing latest instrumental developments and applications of EMEs [8–13].

Extraction devices employed in EMEs are usually down-scaled to be compatible with low volumes of acceptor and donor solutions, which has a direct consequence on their instrumental set-up. Working electrodes are therefore placed into acceptor/donor solutions and electrode reactions associated with the extraction process take place directly in the solutions. Depending on EME variables (e.g., volume of the solutions, extraction time and electric current), considerable concentrations of electrolytic by-products (OH^- and H^+ ions) may be produced in acceptor and donor solutions and affect their pH values [14]. The variations in pH values may be significant especially for acceptor solutions; their volumes are in low μL range and are about two orders of magnitude lower compared to donor solution volumes.

Prior to EME, pH values of acceptor and donor solution are adjusted in order to achieve ionization of analytes in both compartments of the extraction system. These pH adjustments are usually done by addition of low concentrations of strong mineral acids (e.g. 10 mM HCl for basic analytes) or alkaline hydroxides (e.g. 10 mM NaOH for acidic analytes) and ensure electrically induced transfer and preconcentration of charged analytes from donor into acceptor solution. However, if pH value of acceptor solution changes during EME due to production of electrolysis by-products, some of the transferred analytes may lose their charge (depending on their pK_a values). They will not be pushed by electrical field to the respective electrode anymore and as a consequence, the neutral analytes will be diffusively back-extracted into supported liquid membrane (SLM) and/or donor solution. Their concentrations in acceptor solutions will thus decrease and the extraction recoveries will be reduced.

Indeed, a considerable decrease in extraction recovery was observed in many former reports (only the most relevant ones are referenced here [1,15–18]) for EMEs of various analytes at longer EME times. The reasons for the compromised EME performance were, however, not truly examined in any of the previous publications and in order to exactly explain the above process an elaborated study is necessary. Recently, fundamental aspects of electrolysis in EME were described and verified by real-time monitoring of micro-electromembrane extraction (μ-EME) of acid-base indicators [14]. Colour changes of the indicators associated with electrolytically produced OH^- and H^+ ions in catholytes and anolytes, respectively, clearly demonstrated the detrimental effect of electrolysis on pH values of the respective solutions. Rapid variations in pH values of the aqueous solutions were reported for extractions at standard μ-EME conditions. Preliminary results for a model basic drug papaverine have also revealed that electrolysis has a direct effect on its quantitative EME transfer. From the above mentioned literature, it is evident that the effects induced by electrolysis in EME are strong and very complex. Till now, there is no publication available offering systematic investigation and explanation of the electrolysis phenomena on quantitative aspects of EME.

In this contribution, a comprehensive study is presented that summarizes the effects of electrolytically induced changes in operational solutions on EME performance for acidic and basic analytes. For each group of analytes, several compounds with different pK_a values were selected and various acceptor solutions with different compositions and pH values were chosen. Characterization of the EME systems was based on examination of various operational parameters and quantities, such as, pH values, electric currents, electric charges, concentrations of electrolytically produced H^+ and OH^- ions, and concentrations of transferred analytes. The quantitative parameter of key importance was extraction recovery, which was employed as the unique measure of the EME performance. Correlation between the electric charges that passed through the EME system and variations in acceptor solution pH values has also been investigated as well as relation between the decrease in extraction recoveries of the analytes, their pK_a values and the observed acceptor solution pH values.

2. Materials and methods

2.1. Reagents and standard solutions

All chemicals were of reagent grade and deionized (DI) water with resistivity higher than 18 MΩ cm was used throughout. Stock solutions of substituted phenols (10,000 μg mL^{-1}): phenol, pK_a 10.0; 4-chlorophenol (4-CP), pK_a 9.4; pentachlorophenol (PCP), pK_a 4.7; 2,6-dinitrophenol (2,6-DNP), pK_a 3.7 (Sigma, Steinheim, Germany) and picric acid, pK_a 0.4 (Pliva-Lachema, Brno, Czech Republic) were prepared in pure methanol (Sigma). Picric acid is an explosive and should be treated with special care. Standard solutions for capillary electrophoresis (CE) measurements were prepared from these stock solutions and were diluted with DI water (10–350 μg mL^{-1} of each phenol). Stock solutions of basic drugs (1000 μg mL^{-1}): nortriptyline hydrochloride, pK_a 9.7; procaine hydrochloride, pK_a 9.0 and papaverine hydrochloride, pK_a 5.9 (Sigma) were prepared in pure methanol. Standard solutions for CE measurements were prepared from these stock solutions and were diluted with DI water (1–50 μg mL^{-1} of each drug). Chemical structures, pK_a values and log P values of all analytes are summarized in Table S1 in Supplementary data. All stock and standard solutions were stored at the temperature of 4 °C.

Stock solutions of cesium hydroxide monohydrate (100 mM, Fluka, Buchs, Switzerland), ethanolamine (1 M, Sigma), acetic acid, formic acid (1 M, Fluka), HCl (1 M, Lach:Ner, Neratovice, Czech Republic) and buffer solution consisting of 40 mM $Na_3PO_4 \cdot 10\ H_2O$ and 10 mM NaOH (Fluka) at pH 12.31 were prepared from pure chemicals and were diluted with DI water. Donor solutions for EMEs of substituted phenols were prepared by mixing the phenols with DI water and by addition of KOH (Lach:Ner) to the final concentration of 0.5 mM KOH (pH = 9.74). Donor solutions for EMEs of basic drugs were prepared by mixing the analytes with DI water and by addition of HCl to the final concentration of 10 mM HCl (pH = 1.96). 1-Ethyl-2-nitrobenzene (ENB) was obtained from Fluka and was of highest available purity (≥98%). The solvent was used without any further purification.

2.2. Electromembrane extraction

Schematic drawing of the EME device is depicted in Fig. 1. One