The effects of electrolysis on operational solutions in electromembrane extraction: The role of acceptor solution

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ABSTRACT

Fundamental operational principle and instrumental set-up of electromembrane extraction (EME) suggest that electrolysis may play an important role in this recently developed micro-extraction technique. In the present study, the effect of electrolysis in EME is described comprehensively for the first time and it is demonstrated that electrolysis considerably influences EME performance. Micro-electromembrane extraction (μ-EME) across free liquid membrane formed by 1-pentanol was utilized for real-time monitoring of the electrolytically induced changes in composition of μ-EME solutions. These changes were visualized with a set of acid–base indicators. Changes in colours of their aqueous solutions revealed serious variations in their pH values, which occurred within seconds to minutes of the μ-EME process. Variations of up to eight pH units were observed for indicator solutions initially prepared in 1, 5 and 10 mM hydrochloric acid. No or only negligible pH changes (less than 0.15 pH unit) were observed for indicator solutions prepared in 50 and 100 mM acetic acid demonstrating that initial composition of the aqueous solutions was the crucial parameter. These results were also confirmed by theoretical calculations of maximum pH variations in the solutions, which were based on total electric charge transfers measured in the μ-EME systems, and by exact measurements of their pH values after μ-EMEs. Acceptor solutions that, in the current practice, consist predominantly of low concentrations of strong mineral acids or alkali hydroxides may thus not always ensure adequate EME performance, which was manifested by decrease in extraction recoveries of a basic drug papaverine. A suitable remedy to the observed effects is the application of acceptor solutions containing high concentrations of weak acids or bases. These solutions not only eliminate the decrease in recoveries but also serve well as matrices of extracted samples for subsequent analysis by capillary electrophoresis.

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1. Introduction

During the last two decades, micro-extraction sample pre-treatment techniques have been shown suitable for clean-up and preconcentration of samples with complex matrices [1–11]. Among these techniques, electromembrane extraction (EME) has gained significant attention especially due to its unprecedented extraction speed, instrumental simplicity, low costs, minimum environmental impact, applicability to various samples/analytes and compatibility with all major separation techniques [12–14].

In EME, charged analytes from an aqueous donor solution are transferred across a thin layer of a water immiscible solvent into an aqueous acceptor solution by the action of electric potential difference. The solvent is usually anchored in nano-pores of an inert supporting material and forms a supported liquid membrane (SLM). Based on the composition of the solvent, unique SLMs can be formed, which act as highly selective phase interfaces, enable transfer of particular analytes from donor into acceptor solution and simultaneously eliminate transfer of bulk matrix components.

Theoretical aspects of EME were considered several times in the past. Gjelstad at al. [15] hypothesized similarity between the extraction process in EME and iontophoretic transport of charged species across cellular membranes in human bodies based on Nernst–Planck flux equation. The major parameters affecting kinetics of EME, and thus the flux of ions across SLM, were electric potential difference, ion balance between donor and acceptor solution and extraction temperature. In a follow-up paper, Gjelstad at al. [16] suggested that the main limiting factor in EME kinetics was migration velocity of ions across the SLM. Ionization of analytes in donor solutions was not found essential since the main driving force that transports the analytes to the donor/SLM interface was diffusion and convection provided by stirring. Indeed, EMEs of

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basic drugs using donor solution with pH values 4–11 resulted into comparable extraction performances.

Šlampová et al. [17] proposed that EME performance was dependent on the electric regime applied. In EMEs at constant voltage, electric currents varied for non-uniform extraction units based on the Ohm's law since the total electrical resistance of the EME system is given by the SLM conductivity. Total electric charges passed through the system were thus different even for slightly non-uniform SLMs of individual extraction units and consequently total amounts of ions transferred across the SLMs were different in accordance with Faraday's law. A significantly better performance (in terms of repeatability) was thus achieved when EMEs were carried out at stabilized constant electric current instead of constant electric voltage.

Rezazadeh at al. [18] demonstrated that application of pulsed electrical potential also improved performance of EME. In this approach, extraction voltage was applied for short periods (pulses), which were interspaced with even shorter outage periods when no voltage was applied. The double layer of matrix ions, which was formed at the donor/SLM and SLM/acceptor interfaces during the pulse any may limit the transfer of analytes across SLM, was disrupted during the outage period due to convection. The outage period was short enough to avoid diffusive extraction of the transferred analytes back into the donor solution. Better extraction efficiency and higher stability in extractions of samples with complex matrix were achieved compared to conventional EME. Electronic simulation of EME describing SLM as a simple equivalent circuitry consisting of a resistor and low leakage capacitor in series was described recently by Moazami et al. [19].

Although a number of theoretical aspects of EME were investigated in the past, the most obvious one, electrolysis, was not truly considered so far. The instrumental set-up of currently used EME devices necessitates immersion of working electrodes into donor and acceptor solutions and thus electrode reactions take place directly in the solutions. Moreover, typical operating conditions of EME systems (i.e., acceptor solution composition and volume: 10 mM HCl or NaOH and 10–20 μL, electric current: 1–100 μA, extraction time: 5–30 min) suggest that electrolysis may significantly affect composition and thus pH values of acceptor solutions. The need for comprehensive examination of the effects of electrolysis in EMEs is further supported by earlier findings in capillary electrophoresis (CE) demonstrating considerable pH changes of background electrolyte solutions as a consequence of electrolysis during CE runs [20–23].

The role of acceptor solution in EME is very complex as it stems from both, its function in EME as well as in subsequent CE analysis. Acceptor solution serves (i) as a collector of substances crossing the liquid membrane in the direction from donor to acceptor solution, (ii) as the source of counter-ions in order to close the electric circuit and (iii) as the sample matrix for subsequent analysis (after EME is finished) by an analytical, usually chromatographic or electrophoretic, method. The parameters of acceptor solutions, which can be optionally set, are chemical composition and volume. The selection of these parameters has been already given adequate attention and basic rules have been sufficiently developed [12–14].

There is, however, an important problem, which has not been given sufficient attention till now, i.e., description and explanation of the behaviour of the acceptor solution, which is induced by electrolysis during EME. Furthermore, the effect of electrolysis on qualitative and quantitative results of EME, especially on recovery of the extracted analytes, has been overlooked till now and researchers involved in EME mostly did not realize that such a problem exists at all.

This contribution presents a fundamental study on the effects of electrolysis in EME, which employs the recently developed micro-electromembrane extraction (μ-EME) across free liquid membrane

(FLM) [24,25]. Effects of electrolysis are examined with aqueous solutions of selected acid–base indicators, that can be applied in a wide pH range, and by continuous monitoring of their colour changes, which are associated with electrolytically induced variations in pH values of the solutions. Additionally, the disturbing effects, which are induced by electrolysis in solutions with μL volumes, are described and proposals for their efficient elimination are presented. The described effects are confirmed by experiments and theoretical calculations presented in Supplementary data. Actually, the problem of the recovery decrease in EME of papaverine is demonstrated, explanation of the observed effects is given and proposal for the remedy of the problem is presented.

2. Materials and methods

All chemicals were of reagent grade. Deionized (DI) water with resistivity higher than $18\,M\Omega\,cm$ was prepared by using a mixed-bed ion exchanger water purification system G 7749 (Miele, Gütersloh, Germany). Stock solutions of acid–base indicators (10 mM, Pliva-Lachema, Brno, Czech Republic) were prepared from pure chemicals. The following indicators were used in this study: congo red (3,3′-([1,1′-biphenyl]-4,4′-diyl)bis(4-aminonaphthalene-1-sulfonic acid) disodium salt) with a colour change from blue to red at pH 3–5; brilliant yellow (2,2′-(1,2-ethenediyl)bis[5-[(4-hydroxyphenyl)azo]-benzenesulfonic acid disodium salt) with a colour change from yellow to red at pH 6.4–8.0 and phenolphthalein (3,3-bis(4-hydroxyphenyl)-1(3H)-isobenzofuranone) with a colour change from colourless to pink at pH 8–10 [26]. Standard solutions of the indicators (1 mM) were freshly prepared from stock solutions and were diluted with DI water, hydrochloric acid or acetic acid. Stock solutions of the acids (1 M) were prepared from 36% HCl (Lach:Ner, Neratovice, Czech Republic) and 99.8% acetic acid (Fluka, Buchs, Switzerland), respectively, and were kept at room temperature. 1-pentanol (Fluka, ≥99%) was used as FLM in all μ-EME experiments.

Stock solution of papaverine hydrochloride (1000 μg/mL, Sigma, Steinheim, Germany) was prepared in pure methanol (Sigma). Standard solutions for CE measurements were prepared from the stock solution and were diluted with DI water to final concentrations of 1–50 μg/mL of papaverine. Stock solutions of 1 M formic acid (Fluka) and HCl were prepared in DI water. Donor solutions for EMEs of papaverine (1 μg/mL) were prepared by mixing the stock solution with DI water and by addition of HCl to the final concentration of 10 mM HCl (pH 1.98). All solutions were stored at the temperature of 4 °C. 1-Ethyl-2-nitrobenzene (ENB) for formation of SLMs was obtained from Fluka (≥98%) and was used in all EME experiments.

Extraction units for visual monitoring of μ-EMEs were made of a chemically inert perfluoroalkoxy tubing (PFA, 1.0 mm/1.6 mm ID/OD, Part No. JR-T-4007, Vici-Jour, Schenkon, Switzerland). The PFA tubing was cut into 20 mm long units and 0.5–10 μL micropipette (Eppendorf, Hamburg, Germany) fitted with 0.1–10 μL micropipette tip (epT.I.P.S., Eppendorf) was used to fill the extraction unit with solutions. 1.5 μL of DI water (anolyte), 1.5 μL of 1-pentanol (acting as the FLM) and 1.5 μL of aqueous solution containing acid–base indicator (catholyte) were successively pipetted into the unit to form a three-phase extraction system. Extraction unit filled with the three respective solutions is depicted in Fig. 1.

μ-EMEs across FLMs were performed by a d.c. power supply ES 0300-0.45 (Delta Elektronika, Zierikzee, Netherlands). Two 0.25 mm tubular platinum wires (99.95%, Advent, Oxford, England) were used as electrodes. For μ-EMEs of the acid–base indicator solutions, cathode was placed into the indicator solution and anode into DI water. Electric current in the μ-EME system was