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CONTENTS

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LIQUID-PHASE MICROEXTRACTION IN A SINGLE HOLLOW FIBRE - DETERMINATION OF MASS TRANSFER COEFFICIENT

T. M. Trtić-Petrović[1], K. R. Kumrić[1],T. Vladisavljević[2],
J. S. Đorđević[1], J. Åke Jönsson[3]

[1]Laboratory of Physics, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia, [2]Loughborough University, Department of Chemical Engineering, Leicestershire UK, [3]Center for Analysis and Synthesis, Department of Chemistry, Lund University, Sweden

Abstract

In this study, the mass transfer coefficient of two local anesthetics in liquid-phase microextraction (LPME), which is performed in a single hollow fibre, was investigated. Previously developed mathematical model has been applied for the determination of the overall mass transfer coefficient based on the acceptor phase, K_A, in an unsteady-state LPME [1].

Introduction

Miniaturized LPME has been developed using flat or hollow fibre membrane and applied to concentrate analytes prior to chromatographic analysis [2]. Recently, an alternative concept of unsteady-state LPME in a single hollow fibre (HF-LPME) has been introduced [3] and focused mainly on sample preparation and equilibrium sampling.

The quantification of mass transport coefficients in LPME is important for a proper design and operation of the process and for the purpose of identification of rate limiting steps during mass transfer of solute(s) through the membrane. The overall mass transfer coefficient based on the acceptor phase, K_A, in HF-LPME has been estimated from time-dependent concentration of extracted analyte in the acceptor phase while maintaining a constant analyte concentration in the donor phase:

$$K_A = -\frac{V_A}{A}\frac{\partial}{\partial t}\left[\ln\left(\frac{C_A^* - C_A}{C_A^*}\right)\right] \quad (1)$$

where V_A is the volume of the acceptor phase, A is the area of the hollow fibre wall, and C_A^* and C_A is the equilibrium and actual concentration of the analyte in the acceptor phase in time t. The proposed conditions can be achieved either using a relatively large volume of the donor phase or tuning the extraction conditions in order to get a very low enrichment factor, so that the analyte concentration in the bulk of the donor phase can be regarded as a constant. The purpose of this work was to determinate the overall mass transfer coefficient of the selected drugs in an unsteady-state HF-LPME.

Results and Discussion

The investigated local anesthetics bupivacaine (Bup) and lidocaine (Lid) are amines with the values of the dissociation constants (pK_a) of 8.9 and 8.5, respectively. The equilibrium extraction could be reached by adjusting the pH of the acceptor solution. The stripping of the investigated compounds was complete at the acceptor pH at least 3 pH units below the pK_a value of the analyte. With increasing acceptor pH, the amount of nonextractable form of the amines in the acceptor decreased, the back extraction of the amine decreased and the resistance to the mass transfer in the acceptor phase increased.

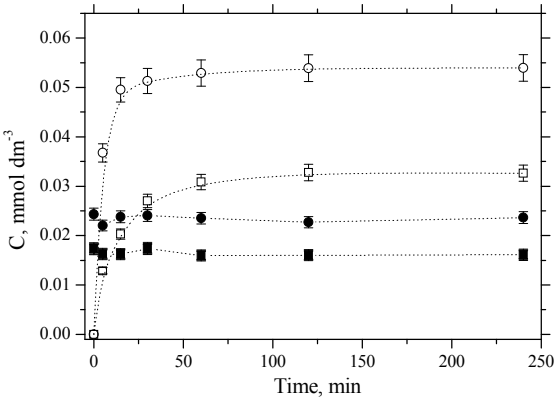

Figure 1. Time dependence of Lid and Bup in the acceptor (C_A) and donor (C_D) phases. Legend: Lid C_D - ●, C_A - ○; Bup C_D - ■, and C_A - □.

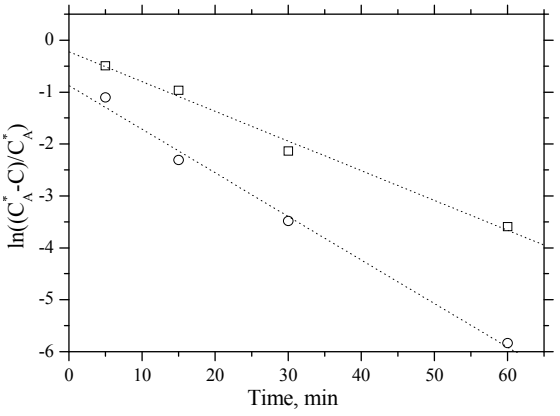

Figure 2. Semi-log plot of the local anesthetics concentration driving force versus time. Legend: ○ - Lid and □ - Bup.

The investigated drugs were extracted in the three phase extraction system [4], from the donor phase (0.067 mol dm^{-3} phosphate buffer at pH 7.5 or blood plasma), through the organic phase placed in the hydrophobic membrane pores (5% TOPO in di-hexyl ether), and finally reextracted into the acceptor phase. The experimental conditions of the acceptor pH can be found in Ref. [3]. Fig. 1 shows the time dependence of the concentration of the investigated drugs in the donor and acceptor phase. Comparing the initial concentration of the drug in the donor phase (0.025 and 0.018 mmol dm^{-3} for Lid and Bup, respectively) and the concentration at certain extraction time, it can be seen that the depletion of the drug from the donor phase was less than 5%, and Eq. (1) can be applied for determination of K_A.

Fig. 2 is a plot of the ratio of concentration driving force (the difference between the equilibrium and actual concentration of the analyte in the acceptor phase) and equilibrium concentration in the acceptor phase versus time for the studied local anaesthetics. The similar dependence was obtained for the extraction

of the local anesthetics from plasma sample. The slope of $\ln[(C_A^* - C_A)/C_A^*]$ vs. t line is equal to $-K_A A/V_A$ and enables K_A to be determined in a batch system under unsteady-state conditions. The calculated values of K_A of the investigated drugs are given in Table 1. The mass transfer coefficient of the drug with higher protein binding (Bup) was higher for extraction from buffer solution than that from plasma solution i.e. K_A was higher for the higher initial drug concentration.

Table 1. The overall mass transfer coefficient of studied local anesthetics.

Compound	Donor	C_D^{in}, mmol dm^{-3}	pH_A	$K_A \times 10^4$, cm min^{-1}
Lidocaine	buffer	0.024	7.2	5.0
Lidocaine	plasma	0.024 ([a]PB 11%)	7.2	5.1
Bupivacaine	buffer	0.017	7.4	3.4
Bupivacaine	plasma	0.017 ([a]PB 69%)	7.4	3.0

[a]PB is protein binding defined and estimated in Ref. [4]

Conclusion

The determination of the overall mass transfer coefficient in HF-LPME under non steady-state conditions was demonstrated in this paper. The results show that the developed mathematical model was successfully applied for determination of K_A.

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