

Optimisation of the conditions for stripping voltammetric analysis at liquid-liquid interfaces supported at micropore arrays. A computational simulation

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Abstract

Micropore membranes have been used to form arrays of micro-interfaces between immiscible electrolyte solutions (μ ITIES) as a basis for the sensing of non-redoxactive ions. Implementation of stripping voltammetry as a sensing method at these arrays of μ ITIES was applied recently to detect drugs and biomolecules at low concentrations. The present study uses computational simulation to investigate the optimum conditions for stripping voltammetric sensing at the μ ITIES array. In this scenario, the diffusion of ions in both the aqueous and the organic phases contributes to the sensing response. The influence of the pre-concentration time, the micropore aspect ratio, the location of the micro-interface within the pore, the ratio of the diffusion coefficients of the analyte ion in the organic and aqueous phases, and the pore wall angle were investigated. The simulations reveal that the accessibility of the micro-interfaces during the pre-concentration period should not be hampered by a recessed interface and that diffusional transport in the phase where the analyte ions are preconcentrated should be minimized. This will ensure that the ions are accumulated within the micro-pores close to the interface and thus be readily available for back-transfer during the stripping process. On the basis of the results, an optimal combination of the examined parameters is proposed, which together improve the stripping voltammetric signal and provide an improvement in the detection limit.

Keywords: ITIES, liquid-liquid interface, stripping voltammetry, computational electrochemistry, simulation.

Introduction

Anodic stripping voltammetry (ASV) is a highly sensitive technique for the determination of trace metals [1, 2]. Cathodic reduction of the target metal ions at a mercury electrode during the pre-concentration step produces a metal amalgam, resulting in concentrations of the metal in the mercury phase which greatly exceed the bulk concentration in the aqueous sample. The metals are then oxidised during an anodic stripping potential scan, resulting in a voltammetric stripping peak. It is the accumulation of the target metals into the mercury working electrode that is responsible for the remarkable detection limits in the low parts per billion (ppb) to high parts per trillion (ppt) range, making anodic stripping analysis a relatively simple but powerful tool for trace metal analysis.

Stripping voltammetric (SV) techniques have also been applied at the interface between two immiscible electrolyte solutions (ITIES) [3-8]. Unlike ASV at mercury working electrodes, in SV experiments at the ITIES the target ions may be cations or anions and do not need to be redox-active. This is because the charge transfer in electrochemistry at the ITIES is the transfer of the target ions and not their reduction or oxidation. Furthermore, hydrophobic as well as hydrophilic ions can be detected, provided that their Gibbs energies of transfer are such that the interfacial transfer occurs within the potential window defined by the transfers of the background electrolyte ions. This widens the range of ions which can be analyzed by SV. Thus a variety of analytes have been detected by SV at aqueous-organic liquid-liquid interfaces, including trace metal ions such as Pb^{2+} , Cd^{2+} , Zn^{2+} and Hg^{2+} [3, 7], biological ions such as acetylcholine [4, 5] and choline [6] cations, and even neutral surfactants [8] (using metal ion-assisted transfer). SV at the ITIES has also been recently applied to the detection of biomolecules such as oligopeptides [9], protein digests [10], drugs (e.g. the beta-blocker propranolol [11, 12]) and inorganic anions like perchlorate [13] and hexafluoroarsenate [14].

Improvement of the detection limit of stripping voltammetry can be based on the following strategy: increase the mass transfer rate, i.e. the interfacial flux, of the analyte from phase 1 to phase 2 during the preconcentration step, while at the same time decreasing the mass transfer of the analyte in phase 2. This leads to an accumulation of the analyte ions in phase 2 close to the interface and these ions are then readily available for stripping back into phase 1, resulting in an increased stripping peak. At the ITIES, this strategy is implemented by miniaturisation of the interface down to the

micron-scale (μ ITIES) or smaller. There are two approaches to establish μ ITIES: either at the tip of a pulled glass pipette or at micropores in a membrane, see [15] and citations therein. In both cases, ion transfer reactions are characterized by an asymmetric diffusion field. With the analyte ions in the aqueous phase and the micropores totally (or almost totally) filled with the organic phase, a spherical diffusion field will be established for the transfer of the analyte ions during pre-concentration step, associated with a high mass transfer coefficient and a steady-state flux. In contrast, the flux within the micropore can be essentially planar, resulting in a reduced mass transfer rate compared to the mass transfer associated with spherical diffusion. Therefore the analyte ions will accumulate within the pore and an increased sensitivity for the stripping process is expected. Furthermore, the accumulation process depends on the pre-concentration time, the pore depth and the ratio of the diffusion coefficients of the target analyte in both phases [16].

Recently, regular arrays of μ ITIES were developed in our laboratory using micropores micromachined into solid-state silicon membranes [17]. Different array designs were realized, with varying number of pores arranged in a hexagonal pattern, pore radii between 5 and 25 μm and pore center-to-center separations between 100 and 1000 μm . The membrane thickness (pore depth) was 100 μm . Cyclic voltammetry (CV) of ion transfer across the μ ITIES confined within such solid-state micropore arrays was studied in detail by comparison of experiments and simulations [18]. Two characteristics of the system were identified which make it suitable for the application of SV: (i) the μ ITIES were practically co-planar with the membrane surface on the aqueous side, i.e. the pores were filled with the organic phase, in this case with 1,6-dichlorocyclohexane gelified by the addition of low molecular weight polyvinyl chloride; and (ii) the diffusion coefficient of a transferring tetraethylammonium ion (TEA^+) in the organogel was ca. 9-times lower than in the aqueous electrolyte phase. Combined with the high aspect ratios $\theta=l/r_a$ of the pores, (where l is the pore depth and r_a the pore radius), the micropore arrays were shown to be an excellent platform for differential pulse stripping voltammetry (DPSV) [16] and were applied to DPSV analysis of drugs [11, 12] and biomolecules [9].

In this report, we present the results of investigations by computer simulation of SV experiments at the μ ITIES array. The influence of parameters such as the interface location within the pore, the pore wall angle, the pre-concentration time and various pore depths and different ratios of diffusion coefficients of the analyte in the aqueous and organic phases were examined. The pore depth and the pore wall angle can be adjusted in the preparation of the solid-state micropore arrays and suggestions for a design optimised for SV analysis are presented.

Theory

A detailed description of the simulation of CV involving ion transfer across ITIES located within micropores was given recently[18]. Here we provide a short summary. Transport is considered by diffusion only, with the time-dependent diffusion equation given in cylindrical coordinates with z and r being the space coordinates[19]. The space coordinates are scaled by the radius r_a of the micropore opening, so that $Z = z/r_a$ and $R = r/r_a$ are the dimensionless coordinates, see Figure 1. The normalised radius and depth of the pore is then given by $R_a = 1$ and $L = l/r_a$. By this definition, the dimensionless depth L of the pore is equal to the pore aspect ratio θ and the parameter L is sufficient to characterise the geometric properties of a single cylindrical pore. Figure 1 illustrates the axial symmetrical computational domain. The location of the liquid-liquid interface within the pore is at $z = m$ and the quantity $M = m/r_a$ marks the dimensionless recess of the interface (for convenience, the quantities L and M are assigned to the absolute values of their Z -coordinate). For $M = 0$ the pore is filled with the organic phase and the interface is co-planar with the upper side of the membrane. For $M = L$, the pore is filled with the aqueous phase and the interface is co-planar with the lower membrane side (see Figure 1). The concentrations are normalised by $C = c/c^{\text{bulk}}$, where c^{bulk} is the bulk concentration of the analyte ions initially present in the aqueous phase. The time t (in seconds) is transformed to the dimensionless time by $\tau = tD_A/r_a^2$, where D_A is the diffusion coefficient of the transferring species in the aqueous phase, which is greater than or equal to D_B , the diffusion coefficient of the same species in the organic phase. A dimensionless scan rate is defined by $\sigma = r_a^2 Fv/(D_A RT)$ where v is the potential scan rate (V s^{-1}) and F , R and T have their usual meaning. The spatial limits of the computational domain, Z_{max} and Z_{min} are estimated from the diffusion layer thickness $6(\tau_{\text{max}})^{1/2}$ developed during a simulated experiment of duration τ_{max} [19]. At Z_{max} and Z_{min} , Dirichlet boundary conditions ($C = 0$ or $C = 1$) are applied for all R . No-flux boundary conditions are applied along the symmetry axis ($R = 0, Z_{\text{min}} < Z < Z_{\text{max}}$) at ($R = R_{\text{max}}, Z_{\text{min}} < Z < Z_{\text{max}}$) and along the surface of the insulator. R_{max} is calculated from the pore centre-to-centre distance of $500 \mu\text{m}$ taking into account the diffusion domain approach for a regular hexagonal array [20, 21]. Membranes with the same center-to-center distance, a pore radius of $26 \mu\text{m}$ and a pore depth (membrane thickness) of $100 \mu\text{m}$ have been employed in recent SV experiments [11, 12, 16]. Simulations revealed a slight diffusion zone overlap at this pore separation for the longest duration of the experiments; however, the effect on the current was negligible [16, 18]. The current at such an array is then simply a multiple of the current of a single pore, as confirmed by comparison to experiments [16, 18].

The kinetics of ion transfer across the ITIES can be treated as a quasi-reversible, first order process with the potential dependence of the rate constants following a Butler-Volmer-type equation [22-24]. Thus, the Butler-Volmer equation, together with the equation of interfacial flux conservation constitutes the boundary conditions at the interface [18]. However, ion transfer across the ITIES was found to be reversible on the time-scale of voltammetric experiments at millimetre-sized interfaces [23, 24] and micro-interfaces [25]. Further decrease of the interface beyond the microscale by employing pipettes with radii of the order 1-10 nm, thus increasing further the mass transfer coefficient, reveal values for k^0 between 2.0 cm s^{-1} and 100 cm s^{-1} for tetraethylammonium transfer across the water|1,2-dichloroethane interface [26] and $\sim 1.0 \text{ cm s}^{-1}$ for the transfer of laurate ions across the water|n-octanol interface [27]. The mass transfer coefficient for micro-interfaces with radii of 10 and 25 μm are of the order of 0.01 cm s^{-1} and 0.005 cm s^{-1} , indicating mass transfer-controlled ion transfer at the micropores. In the present work, a value of $k^0 = 0.5 \text{ cm s}^{-1}$ was assigned to the heterogeneous standard rate constant, effectively resulting in mass transfer control of the ion transfer process at the ITIES. The symmetry factor α was set to 0.5.

The experimental set-up of the cell for investigations of transfer processes at ITIES involves commonly a 4-electrode configuration, with a reference and a counter electrode in each phase. The applied potential waveform for the simulation of linear sweep stripping voltammetry (LSSV) is composed of two parts. In the first part, the Galvani potential difference between the aqueous and organic phases, $\Delta_o^w\phi$, is stepped from a value $\Delta_o^w\phi_{st}$ where no analyte transfers across the ITIES occurs to a potential $\Delta_o^w\phi_{pc}$ resulting in transfer of the analyte from the aqueous phase into the organic phase. This pre-concentration potential, $\Delta_o^w\phi_{pc}$, is held constant for a time τ_c (or t_c in units of seconds). In the second part, a linear potential scan with a scan rate ν from $\Delta_o^w\phi_{pc}$ back to $\Delta_o^w\phi_{st}$ is applied. During the potential scan, the analyte is transferred (stripped) from the organic phase back into the aqueous phase.

In the simulations presented, different diffusion coefficients are assumed for the transferring species in the aqueous and organic phase. The ratio of the diffusion coefficient in the organic and aqueous phase,

$$\gamma = \frac{D_B}{D_A} \quad (1)$$

is used as a parameter in the simulations.

Currents are normalised by the limiting current $i_{\text{lim}} = 4z_iFD_{\text{A}}c^{\text{bulk}}r_{\text{a}}$. The dimensionless current is then given by

$$G = \frac{\pi}{2} \int_0^1 \frac{\partial C_{\text{A}}(R, Z, t)}{\partial Z} \Big|_{Z=M} R dR \quad (2)$$

The gradient in Equation (2) is calculated along the dashed line in Figure 1, ($Z = M, 0 \leq R \leq 1$).

Computational Details

Simulations were performed using the finite element method programme package COMSOL (version 3.5a, COMSOL Ltd., Hertfordshire, UK). Free mesh parameters were used at locations of high concentration gradients. These locations are the points of the orifices at both sides of the pore and along the boundary line where both phases are in contact. Here, the maximal sizes of the triangular elements were set to 0.0002 with a factor of 1.1 for element expansion. These mesh parameters have been tested previously and shown to deliver acceptable error limits ($< 1\%$) in the calculated current [18].

Results and Discussion

The simulations were performed to assess the impact of the variables t_{c} , γ , M , L and the incline angle of the pore wall, as described by the angle α (see Figure 1). For the cationic analyte, the initial and pre-concentration potentials, $\Delta_{\text{o}}^{\text{w}}\phi_{\text{st}}$ and $\Delta_{\text{o}}^{\text{w}}\phi_{\text{pc}}$, were set to 0.3 V and 1.05 V, respectively, and the formal potential of transfer, $\Delta_{\text{o}}^{\text{w}}\phi_i^{\text{o}}$ was 0.58 V. These potential values were chosen according to the transfer potential of TEA^+ which was used as a probe to characterize the transfer behaviour across micro-interface arrays [18] and to investigate the DPSV performance of the micro-interface arrays [16]. The scan rate for the linear sweep stripping was 10 mV s^{-1} .

The influence of the pore aspect ratio

The fabrication process of solid-state membranes enables the arrangement of regular patterns of pores with desired pore radii and pore-to-pore separations, as well as the customisation of the membrane thickness, i.e. the pore depth and thus the pore aspect ratio $\theta = L = l/r_{\text{a}}$. Figure 2A shows the influence of the pore aspect ratio on the stripping peak current G_{p} as a function of the pre-

concentration time. A γ value of 0.115 and interface recess of practically zero was previously estimated by comparison of experiments with simulations [18] for the transfer of tetraethylammonium cations and these values of γ and M were employed in the simulations in Figure 2A. Low aspect ratios lead to smaller stripping signals and for $\theta=1$ and 2 the signal becomes almost independent of the pre-concentration time t_c . At relatively shallow pores, the amount of ions crossing the interface by entering the pore from the aqueous side during the pre-concentration step is quickly balanced by the amount of ions exiting the pore on the opposite side into the organic phase trans-membrane region. In such a case, the concentration of ions accumulating in the pore is independent of the time. Since the stripping peak is related to the concentration of ions present in the pore in the proximity of the interface, no increase with increasing t_c is observed for the lower θ values shown in Figure 2A. However, the deeper the pore, the more ions are accumulated within the pore during pre-concentration and the higher the stripping signal. For the deeper pores, a longer time period is required to reach a balance of the number of ions entering and exiting the pores, which is manifested as an increase of G_p with the pre-concentration time. Membranes with an aspect ratio of 4 (depth 100 μm , radius 25 μm), as used in our laboratory [9, 11, 17, 18], show a saturation of the stripping peak at times around 80 to 90 s [16]. The stripping signal at longer pre-concentration times is improved if pore aspect ratios of up to 8 are used. The gain in stripping signal using even higher pore aspect ratios ($\theta=16$) is small for the range of pre-concentration times shown in Figure 2A.

The influence of the diffusion coefficient of the transferring species

The time for the ions to cross the pore filled with the organic phase depends not only on the pore depth, but also on the diffusion coefficient of the transferring ion in the organic phase. Therefore the influence of the diffusion coefficient ratio γ (Equation (1)) on the stripping peak height is similar to that of the pore aspect ratio. Figure 2B shows simulated stripping peak currents as a function of the pre-concentration time for different γ values. The pore aspect ratio in the simulations was $\theta = 4$ and the interface was at $M = 0$. A γ value close to one is expected, if nitrobenzene or 1,2-dichloroethane, both common solvents in ITIES electrochemistry, are used for the organic phase. In this case, no increase of the stripping peak with increasing t_c is predicted (Figure 2B, $\gamma = 1$). With decreasing γ , i.e. with a decreasing value of the diffusion coefficient of the transferring species in the organic solvent relative to that in the aqueous phase, the absolute G_p values increase, because slower diffusion results in a higher analyte concentration in the pore during the pre-concentration period. Diffusion can be considerably slowed down by increasing the viscosity of the liquid phase.

Therefore the use of organo-gel phases have been established to increase the sensitivity of stripping voltammetry at the ITIES [3, 6-9, 11, 12, 16, 28]. For an organo-gel phase prepared from 1,6-dichlorohexane by addition of low molecular weight polyvinylchloride, we found a ca. 9-fold decrease in the diffusion coefficient for tetraethylammonium ions compared to the aqueous phase, resulting in $\gamma = 0.115$ [18]. As shown in Figure 2B, such a small γ leads to a seven-to-eleven times increase of the stripping peak (depending on the pre-concentration time), compared to a non-gelified organic phase ($\gamma \approx 1$).

The location of the liquid/liquid interface

The accessibility of the interface depends strongly on its position. A recessed position will hamper the diffusion to the interface due to the shielding effect of the surrounding pore walls [29-31] and therefore the steady-state (limiting) current established during the pre-concentration time will decrease with increasing recess length M , as shown in Figure 3A. The normalised steady state current G_{ss} for the interface co-planar with the membrane plane on the aqueous side attains a value of one. In this case $M = 0$ and the pore is filled with the organic phase. For the dimensionless pore length $L = 4$ used in the simulation, $M = 4$ implies that the pore is filled with the aqueous phase and the interface is co-planar with the membrane plane on the organic side. In this configuration, the interface is highly shielded for access of the analyte ions from the aqueous solution and the pre-concentration steady state current is reduced to 0.16. With increasing recess of the interface less ions are transferred during the pre-concentration time and the stripping peak $|G_p|$ is reduced from 2.21 for $M = 0$ down to 0.03 for $M = 4$ (Figure 3B). An additional effect contributes to the decrease of the stripping current with increasing M shown in Figure 3. For a constant L , and increasing M , the inner pore region filled with the organic phase where ions can be accumulated becomes smaller and the distance of the interface to the organic trans-membrane region is diminished, causing dissipation of analyte ions into the organic phase. The effect can be seen by comparing the simulated stripping peak for $M = 4$ and $L = 4$ ($t_c = 90$ s, $\gamma = 0.115$) with the results for the same parameters, but with a pore depth of $L = 8$. Since the shielding effect in both cases is identical, the steady state current during the pre-concentration time is in both cases $G_{ss} = 0.16$. However, for $L = 4$, the stripping peak is $|G_p| = 0.03$, while with $L = 8$, the peak is $|G_p| = 0.32$. However, compared to $|G_p| = 2.21$ for $L = 4$, $M = 0$, the negative effect of a recessed interface on the stripping peak is obvious.

The pore wall angle

The above simulations were all performed for cylindrical shaped pores, i.e. for pores with perpendicular walls where the angle α is 90° (see Figure 1 for the definition of α). However, the shape of the pore can be expected to influence diffusion to and from the interface and hence the effect of the wall angle was investigated. For $\alpha < 90^\circ$, the pore has a conical shape with the pore opening on the aqueous side of the membrane being larger than the pore opening on the organic side, and vice versa for $\alpha > 90^\circ$. For the simulation, the dimensionless radius of the pore on the aqueous side and the depth of the pore were kept constant at $R_a = 1$ and $L = 4$, respectively, and the incline angle α was varied between 78.69° and 101.37° , resulting in dimensionless pore openings on the organic side of the membrane between 0.2 and 1.8. For a micropore of $r_a = 25 \mu\text{m}$ at the organic side, these dimensions translate to $l = 100 \mu\text{m}$, and a pore radius on the aqueous membrane side between 5 and $45 \mu\text{m}$. Figure 4 shows the change of the stripping peak current with the angle of the pore wall. Simulations were performed using $M = 0$, $\gamma = 0.115$ and $t_c = 90\text{s}$. Although the amount of ions transferred from the aqueous into the organic phase during the pre-concentration time is the same in all simulations shown in Figure 4, the incline angle of the pore wall has a strong influence on the stripping of the analyte ions back into the aqueous phase. For $\alpha < 90^\circ$ an increase of the peak current is revealed by Figure 4. After crossing the interface, the diffusion of the analyte towards the far end of the pore and into the organic bulk solution during the pre-concentration period is hindered by the membrane walls which are tapered towards the narrower pore opening on the organic side. This leads to a higher accumulation of the ions within the pore and close to the interface. Consequently, an increase of the peak during the stripping scan is observed. For wall angles of $\alpha > 90^\circ$, once the ions have crossed the interface, diffusional transfer of the analyte in the organic phase away from the interface is increased due to the expansion of the diffusion space. There is less accumulation of the ions in the pore close to the interface and the amount of ions which can be transferred back into the aqueous phase during the stripping scan is reduced, leading to a decrease of the stripping current peak height.

In our current set-up for the analysis of bio-molecules by SV, a pore depth of $100 \mu\text{m}$ and a pore radius of ca. $25 \mu\text{m}$ is used. Furthermore, an organo-gel phase is employed in conjunction with pre-concentration times of ca. 90 s . These optimised conditions can be further improved by using a sloped rather than vertical pore wall. A moderate incline angle of 83° , resulting in a reduction of the radius of the pore opening to $12.5 \mu\text{m}$ on the organic side, will double the peak height of the stripping peak and improve the limit of detection further.

Conclusions

A simulation study of the influence of a number of parameters on linear sweep stripping voltammetry at a μ ITIES array was undertaken. Parameters dependent on both the micropore array design used to form the μ ITIES and the analyte behaviour in the two phases were analysed. The characteristics needed to improve the sensitivity of μ ITIES-based SV were determined. These are:

- The pore should be filled with the organic phase, so that that the ITIES is co-planar with the outer membrane side on the aqueous side;
- The diffusion coefficient of the target analyte ion in the organic phase should be less than in the aqueous phase; this can be achieved by increasing the viscosity of the organic phase.
- The pore depth (membrane thickness) should be large enough to prevent dissipation of the analyte ions into trans-membrane region of the organic phase following their extraction into that phase during the pre-concentration step.
- The pore walls should be tapered towards the organic side of the organic side of the membrane, so as to restrict diffusion away from the interface on the organic side.

Furthermore, the number of pores in the array should be high but diffusion zone overlap should be avoided to ensure high current density during the pre-concentration period.

While this report was restricted to the optimization of the voltammetric stripping signal for ions present in the aqueous phase, the inverse case of analyte ions present initially in the organic phase can be treated analogously. From an experimental point of view, the wetting properties of the membrane walls have to be altered to allow the pore to be filled with the aqueous electrolyte. This can be achieved by suitable chemical treatment [32, 33]. While a non-gelified organic phase should be employed, the viscosity of the aqueous phase should be increased, for example by addition of sucrose [34].

Acknowledgements.

The authors thank Science Foundation Ireland for support (grant number 07/IN.1/B967).

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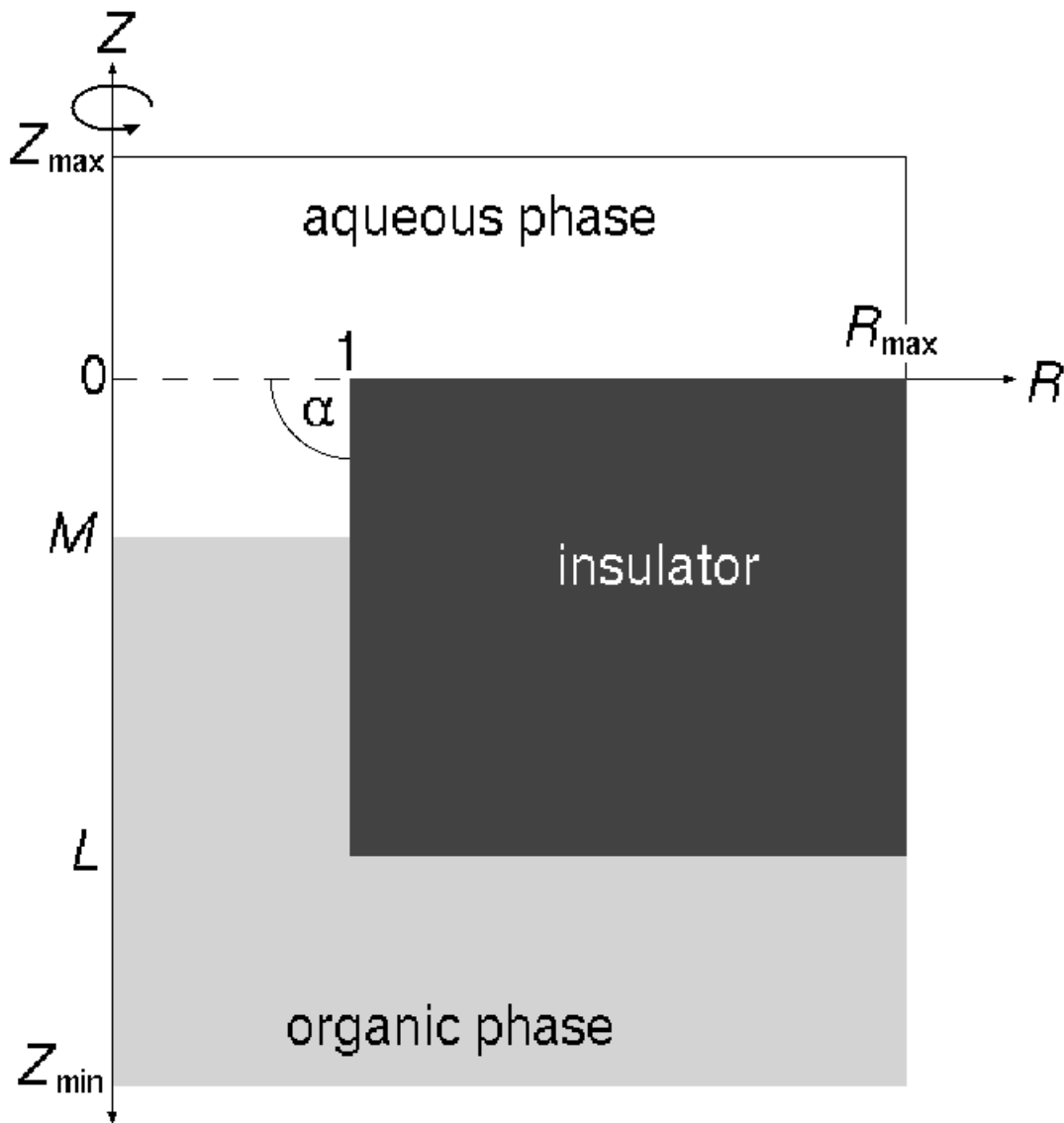


Figure 1. Axial symmetric computational domain (not to scale) for the simulation of liquid-liquid interfaces confined within micropores. The rotational symmetry is indicated by the arrow around the axis of symmetry (Z -axis). L denotes the depth of the micropore and M the location of the interface. The incline of the pore wall is given by the angle α .

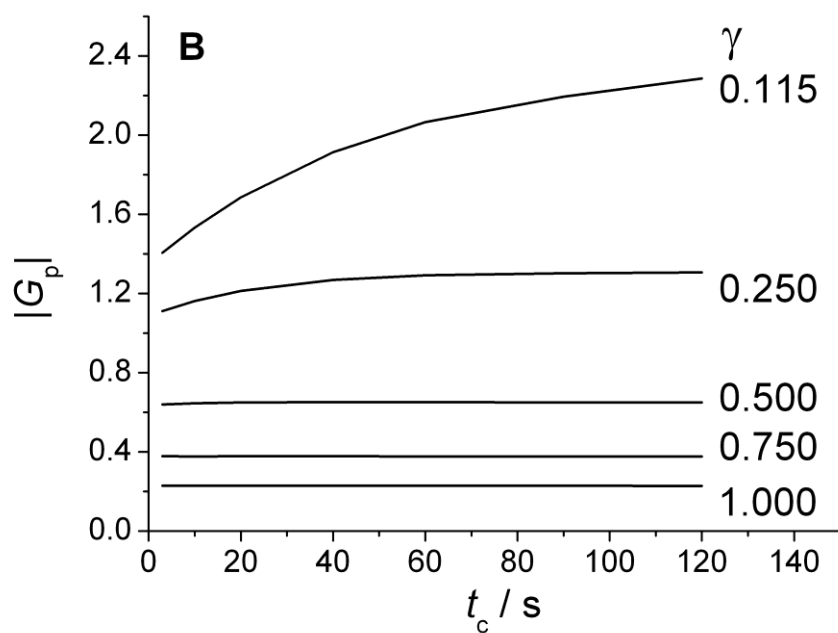
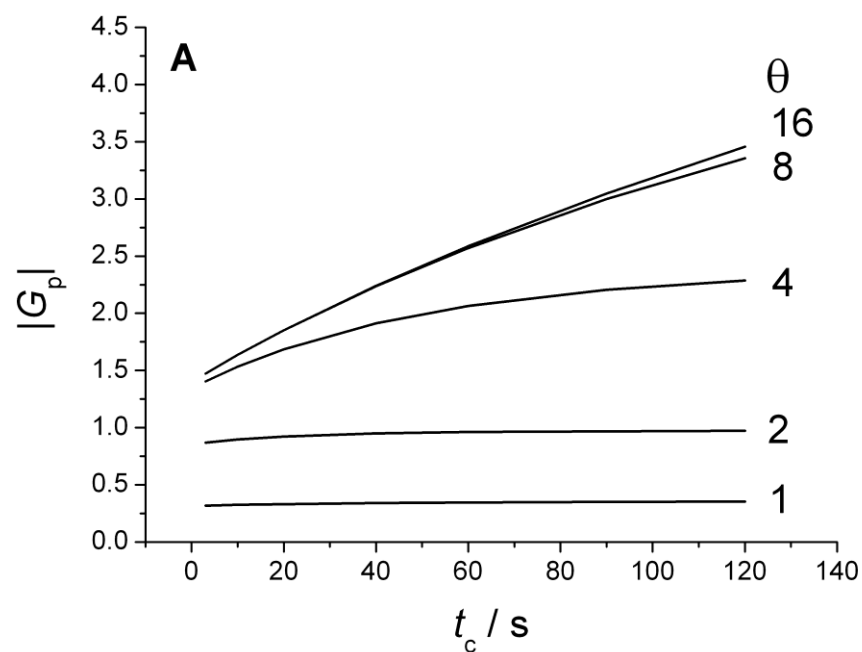


Figure 2. Variation of the stripping peak currents with the pre-concentration time t_c . **A:** Influence of the pore aspect ratio θ . A γ value of 0.115 was used. **B:** The influence of the diffusion coefficient ratio of the transferring species in the organic and aqueous phase, $\gamma = D_B/D_A$. The pore aspect ratio was $\theta = l/r_a = 4$.

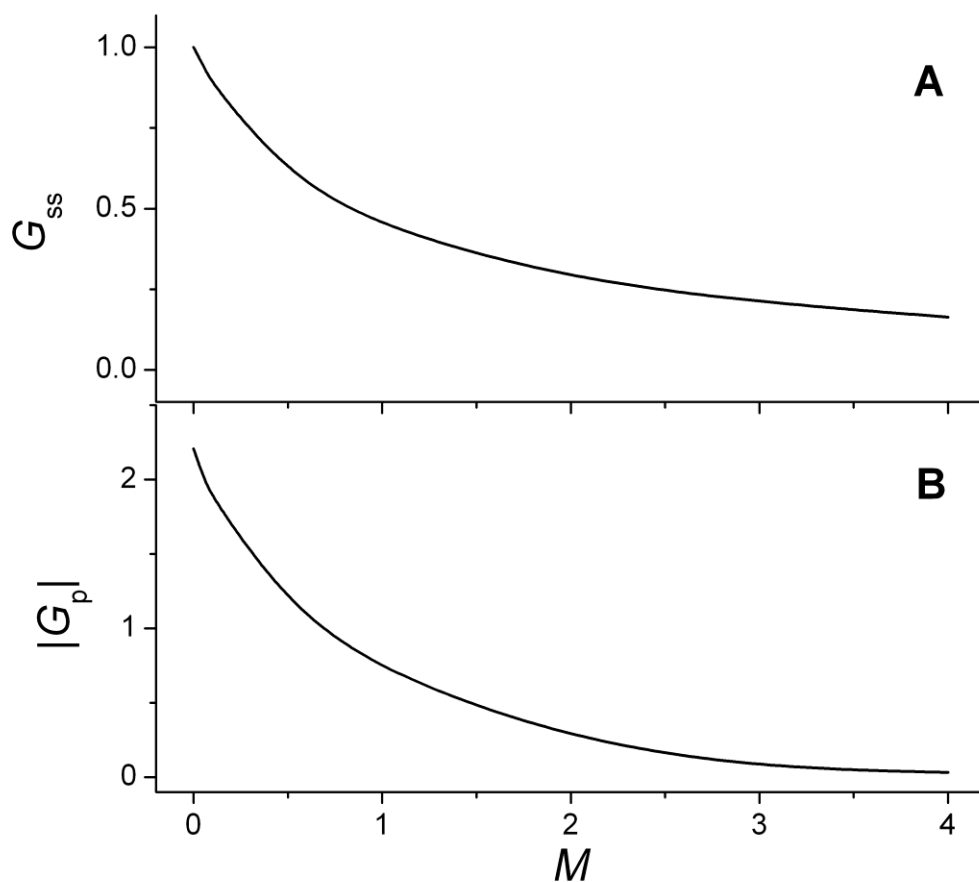


Figure 3. A: Variation of the normalised steady state current attained during the pre-concentration period with increasing normalised recess M of the interface between the aqueous and organic phase; $\theta=4$, $\gamma=0.115$, $t_c=90$ s. **B:** the corresponding current peak of the stripping scan as a function of the normalised recess value.

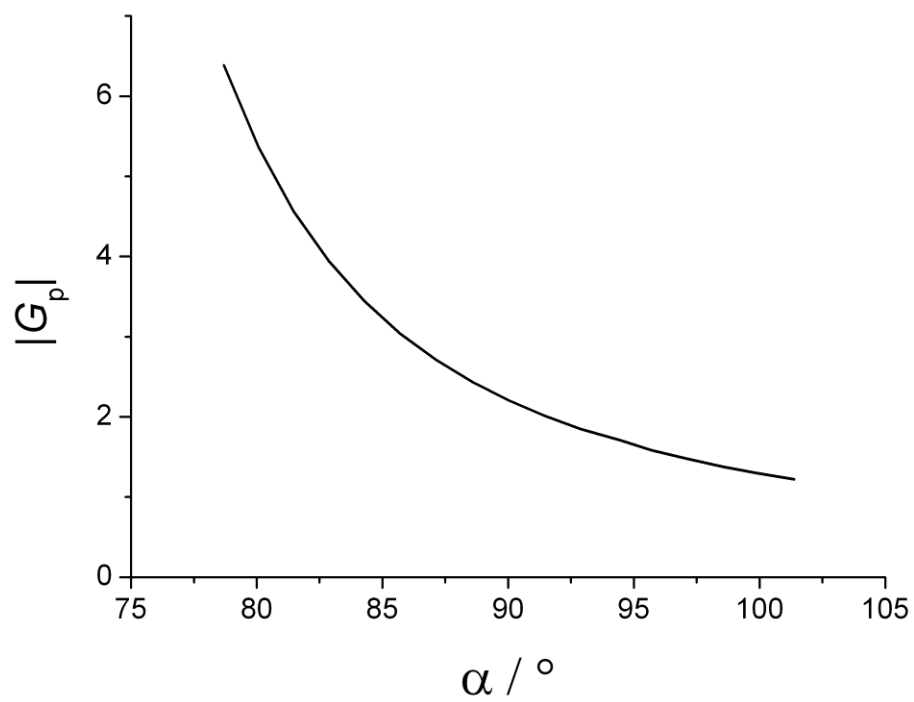


Figure 4. Dependence of the stripping peak current on the incline angle α of the pore wall (see Figure 1). Pre-concentration time = 90 s, $\gamma=0.115$ and $\theta=4$.