

Lab on a Chip

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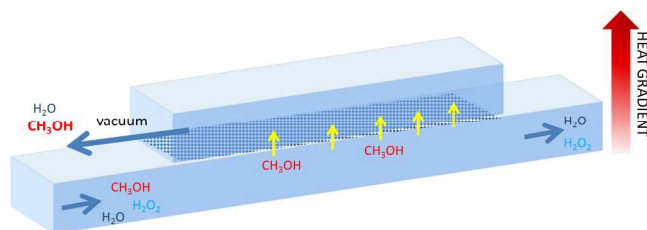
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Hydrogen peroxide concentration by pervaporation of a ternary liquid solution in microfluidics

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ARTICLE

Hydrogen peroxide concentration by pervaporation of a ternary liquid solution in microfluidics

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Pervaporation in a microfluidic device is performed on liquid ternary solutions of hydrogen peroxide/water/methanol in order to concentrate hydrogen peroxide (H₂O₂) by removing methanol. The quantitative analysis of the pervaporation of solutions with different initial compositions is performed, varying the operating temperature of the microfluidic device. Experimental results together with a mathematical model of the separation process are used to understand the effect of the operating conditions on the microfluidic device efficiency. The parameters influencing significantly the performance of pervaporation in the microfluidic device are determined and the limitations of the process are discussed. For the analysed system, the operating temperature of the chip has to be below the temperature at which H₂O₂ decomposes. Therefore, the choice of an adequate reduced operating pressure is required, depending on the expected separation efficiency.

1. Introduction

Due to its strong oxidizing properties, hydrogen peroxide (H₂O₂) is widely used in industry for bleaching, water treatment and therapeutic purposes. Most of its production is made through an optimized Riedl-Pfleiderer process,¹ the so-called anthraquinone process. This process allows the preparation of concentrated solution up to 70 wt% in H₂O₂ but faces problems with effective quinone recycling and formation of by-products which have to be disposed. New applications such as medical tool sterilization or cleaning of microelectronic supports require highly concentrated H₂O₂ solutions. However, the use of these solutions is only possible if they are produced on-site, as it is hazardous to transport H₂O₂ solutions at concentrations higher than 30%. In that context, the on-site production of H₂O₂ by direct synthesis using a microfluidic process has become an active research topic,^{2,3} as it is cost-effective, sustainable and offers the possibility to produce highly concentrated H₂O₂ on demand. Moreover, such a microfluidic process would be an efficient laboratory tool, allowing for instance a rapid screening of operating conditions (pressure, temperature, nature of the catalyst...) to increase the efficiency of the H₂O₂ production reaction, with the use of a limited amount of reactants and catalysts.

Ideally, a microfluidic process for H₂O₂ production would be composed of a chip with interconnected modules dedicated to the production of H₂O₂ and its purification. One of the crucial modules in such a microfluidic process is to obtain, after the reaction, concentrated H₂O₂ by separating it from the other

liquid components (by-products and solvents) present in the process. Pervaporation in microfluidic device seems to be a good method for such a separation as explained below.

Pervaporation is a membrane separation process that is an energy efficient combination of permeation and evaporation.⁴ It is used to remove volatile compounds out of solutions. By creating a vacuum (vacuum pervaporation) or introducing a flow of inert gas (purge gas pervaporation) on one side of a dense (non porous) membrane, volatile compounds in a liquid flow on the other side of the membrane will tend to diffuse through this membrane.

Purge gas pervaporation microfluidic devices were used to concentrate various aqueous solutions via pervaporation of water through a PDMS membrane, in order to study phase diagrams, either steady or out-of-equilibrium,⁵ or the kinetics of such a pervaporation process.⁶ In these studies, binary aqueous solutions were considered.

Separation methods similar to pervaporation were already investigated for several liquid solutions, using different types of microfluidic devices.⁷⁻⁹ Hartman *et al.*⁷ used distillation in microfluidics for binary organic solutions separation. Their device consisted of a capillary in which vapour-liquid equilibrium was reached using segmented flow and a porous membrane to separate the vapour and the liquid flows, using capillary forces. Zhang *et al.*⁸ designed a multi-layered chip for vacuum distillation of H₂O-MeOH solutions, using a temperature gradient. In the work of Adiche and Sundmacher,⁹

the distillation of H₂O/MeOH solutions in microfluidics was studied with the use of different porous membranes.

Because gaseous H₂ and O₂, the reagents for the production of H₂O₂, have a larger solubility in liquid methanol (MeOH) than in water, we foresee that the next generation of chips for the direct synthesis of H₂O₂ will involve the use of MeOH as a co-solvent (with H₂O). After reaction, H₂O₂ and H₂O will have to be separated from MeOH that is undesirable for some applications but still tolerated at very low concentrations of about 1%.

In the present manuscript, we report the use of microfluidic chip for the concentration of H₂O, using pervaporation, in ternary solutions of H₂O₂, MeOH and H₂O. These liquid solutions are processed through a chip designed and developed in our lab. This chip is built as a multi-layer device, as represented in Fig. 1. The key element of this device is the dense membrane¹⁰ situated in-between a liquid channel and a vapour channel in contact, respectively, with a cooling and a heating plate. The liquid solution is flowing through the liquid channel and the different components of the solution can diffuse through the membrane to reach the vapour channel. According to the relative volatility of the components considered in this work, such a system should allow to concentrate H₂O₂ in the liquid solution.

We first present the materials and methods (section 2). As compared to previous works for the separation in microfluidics, no segmented flows in the liquid channel or inert gas flow in the vapour channel are used, and our setup combine vacuum and a temperature gradient as driving forces for the diffusion through the membrane. To the best of our knowledge, it is the first example of a microfluidic device where the pervaporation of a liquid ternary solution is analysed and it is the first attempt of concentration of a solution containing H₂O₂, using microfluidic technology.

A quantitative analysis, using Nuclear Magnetic Resonance (NMR), of the composition of the phases[†] exiting the chip are realized, for various operating temperature of the chip and various compositions of the liquid solution introduced in the chip. Experimental results together with a mathematical model of the process are then used to understand the effect of the operating conditions on the separation process efficiency (section 3). The parameters influencing significantly the performance of the pervaporation in the chip are determined and the limitations of the process are discussed (section 4).

2. Materials and Methods

2.1 Materials

MeOH (HPLC grade) and a liquid solution of H₂O₂ (30 wt%) in H₂O are purchased from Sigma-Aldrich. Hexamethyldisilazane is purchased from Fluka Analytical. They are used as received. A liquid solution of H₂O₂ (60 wt %) in H₂O is received from Solvay company. Poly(dimethylsiloxane) PDMS is prepared from Sylgard 184, Dow Corning.

2.2 Preparation of the microfluidic device

Fabrication of the device is done using soft lithography. Two 4-inch silicon wafers are patterned by exposing a layer of photoresist resin (SU8-2150, MicroChem) to UV light, using the UV-KUB-2 insulator from Kloé company, through a high-resolution transparency mask containing the two-dimensional designs of the microchannel circuits (one for the liquid channel and one for the vapour channel). These patterned wafers are subsequently used as a mold to replicate the structure in PDMS layer of 4 mm thickness. Our device is built up from two layers of PDMS, sandwiching a PDMS membrane, which are prepared using a mixture of pre-polymer and a curing agent in a 5:1 ratio by weight and cured at 70 degrees during 2 hours for high cross-linking. The layers are bonded to the membrane after 30 sec. exposure in a plasma chamber (Harrick).

2.3 Preparation of the membrane

The PDMS membrane is prepared by spincoating a PDMS (prepolymer and curing agent in a 10:1 ratio by weight) layer on a silicon wafer silanized with hexamethyldisilazane, and baked at 70°C for 2 hours. The membrane thickness of 170 μm is measured with a 3D laser microscopy Keyence VK-X200. It is a dense membrane, permeable to H₂O, H₂O₂, MeOH.¹⁰⁻¹³ According to Bell *et al.*¹², the permeability coefficients for H₂O and MeOH in PDMS are of comparable values. Furthermore, the permeability of H₂O₂ is assumed to be identical to the permeability of H₂O. Consequently, it is the relative volatility of these three components that is responsible for the efficiency of the separation process using the microfluidic device.

2.4 Building of the chip

Membranes with different composition (PTFE,⁸ PES, and PVDF) were previously tested for membrane distillation of MeOH/H₂O solutions.⁹ In the microdevices described, membranes were incorporated and fixed by mechanical screwing, which caused problem of leakage. In our setup, we use a membrane made of PDMS as it is commonly used in microengineering.¹⁰ Since our microchannels are also imprinted within PDMS, it allows a tight and hermetic connection with the membrane through plasma bonding. The compatibility of PDMS with MeOH solution has also been tested in our work and elsewhere.¹⁴

Dimensions of the microchannels have to be carefully chosen to ensure an efficient mass transfer of the most volatile compound from the liquid channel to the vapour channel. The liquid channel has a width of 300 μm and the vapour channel has a width of 500 μm. This size difference guarantees that the vapour channel entirely overlap the liquid channel. With this approach, we prevent the formation of dead zones (due to misalignment), i.e. areas where there is no exchange possible through the membrane from the liquid to the vapour channel. A careful alignment of the vapour channel with the liquid channel is required and it is achieved in such a way that the bottom layer (with the liquid channel) is first bonded to the PDMS membrane. Then the top PDMS layer (with the vapour channel) is bonded to the other side of the membrane.

The liquid solution of H_2O , MeOH and H_2O_2 is injected within the liquid channel with the help of a syringe pump whereas partial vacuum is applied to the vapour channel allowing the collection of the vapour condensate within a trap dipped in ice. Flows in microchannels are generally laminar, which means that solvent

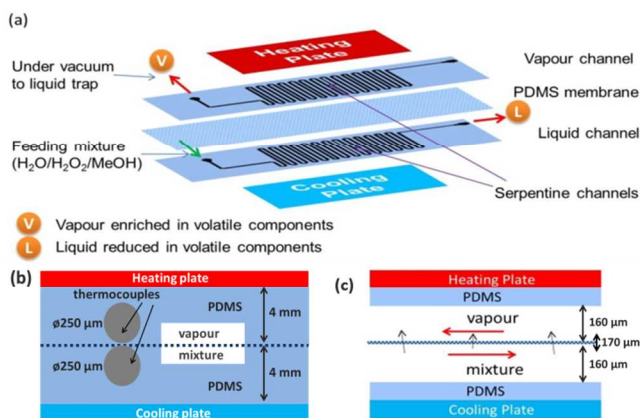


Fig. 1 Scheme of the device: (a) general overview, (b) cross section, (c) side view. Sketches are not at scale.

molecules can only move in a direction transverse to the direction of the flow by diffusion. Based on the diffusion coefficient of MeOH (most volatile component) in H_2O ($1.014 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 25°C for 0.28 mole fraction of MeOH),⁸ we deduced that the liquid microchannel, which is $160 \mu\text{m}$ high, $300 \mu\text{m}$ wide and 90 cm long, ensures that, at a flow rate of $0.1 \mu\text{L/s}$, the process is not limited by diffusion in the liquid channel; the mixing length being about 5 cm .

At the exit of the liquid channel, a more concentrated solution in H_2O_2 should be obtained, as compared to the liquid solution introduced in the chip. Quantification of the concentration in each component is realized thanks to NMR spectroscopy. Composition of the collected condensed vapour is determined to show, on the one hand, what the concentration in each component is and to ensure, on the other hand, that nothing is lost during the process through PDMS walls.

Temperatures ranging from 70 to 90°C , inside the chip, are considered for our set of experiments. Indeed, it has been shown that, at higher temperature, decomposition of H_2O_2 occurs.¹⁷

2.5 Chip operation

The liquid solution is introduced in the liquid channel with the use of a syringe pump at a flow rate of $0.1 \mu\text{L/s}$. The vapour channel is connected to a vacuum pump and a negative pressure of -500 mbar is applied. This has for effect to pump the vapour from the vapour channel in a direction opposite to the flow direction in the liquid channel (see Fig. 1).

2.6 Temperature control

A Peltier element (Thermo Electric Modul TES1 12703S, 27 Watt , 14.5 V , BTS Europe BV) is used as a cooling system. The cold side of the Peltier element is directly put in contact

with the PDMS layer containing the liquid channel. To dissipate the heat, the hot side of the Peltier element is glued to an aluminium plate itself connected to a water cooling system. A heating resistor (24 V , 40 Watt , 14.5 ohm , GBR-666/24/1, TELPOD) is used as a heating device. It is glued to an aluminium plate itself in contact with the PDMS layer containing the vapour channel. The heating plate is positioned on top of the vapour channel such as condensation of the vapour does not occur within the channel. It also ensures an efficient temperature gradient through the chip thanks to the cooling plate located underneath the liquid channel. It is to notice that both temperature elements are only covering the serpentine (see Fig. 1). As mentioned hereafter, only the measurement of the temperature in the liquid channel is needed for the comparison between the experimental data and the model presented in section 3.

We measure precisely the temperature inside the chip with the use of 0.25 mm diameter thermocouples (Omega, TJ36-CASS-010G-12). The thermocouples are placed at different places along the liquid and vapour channels (see Fig. 1). No temperature gradient along the channels is observed, at least within the error of the thermocouples ($\pm 1^\circ\text{C}$). The temperature difference between the liquid channel and the vapour channel is measured to be 2°C for the range of temperatures considered. There can be some inaccuracy in the determination of the temperature in the channels, since the thermocouples are not exactly inside the channels (see Fig. 1) and also since the thermocouples diameter is 0.25 mm ; this is larger than the height of the microchannel (0.16 mm).

2.7 Quantitative analysis

NMR is used to characterize the composition of the output phases of the microfluidic device († Fig. S1-3). H_2O_2 can be characterized by NMR in acetone at low concentrations.¹⁴ For our present measurements, $10 \mu\text{L}$ of the extracted solution is diluted in $590 \mu\text{L}$ of acetone- d_6 . Measurements are performed at -25°C using a 600 MHz Varian instrument. The analysed solutions had a pH around 6. With these conditions, good separation of the signals inherent to H_2O_2 , H_2O and MeOH is obtained. The error of NMR measurement is 5% .

3. Mathematical model

A coordinate x , along the microchannels, is introduced. The value of $x = 0$ at the inlet of the liquid channel (and hence at the outlet of the vapour channel) and $x = L_p$ at the outlet of the liquid channel (and hence at the end of the vapour channel). For our chip $L_p = 0.9 \text{ m}$. For reasons explained hereafter, a flow of inert gas is considered in the developed mathematical model of the chip. This inert gas is thus introduced in the chip at $x = L_p$ and flows with the generated vapour towards $x = 0$. The parameter $L(x)$ (mol/s) is the molar flow rate of liquid at the position x in the liquid channel. The parameter $G(x)$ (mol/s) is the molar flow rate of gas at the position x in the vapour channel. The molar fractions of H_2O , MeOH and H_2O_2 in the liquid at the position x in the liquid channel are written $w_i(x)$,

$m_l(x)$ and $h_l(x)$, respectively. The molar fractions of inert gas, H₂O, MeOH and H₂O₂ in the gas at the position x in the vapour channel are written $i_g(x)$, $w_g(x)$, $m_g(x)$ and $h_g(x)$, respectively.

The following balance equations can be written:

$$w_l(x) + m_l(x) + h_l(x) = 1 \quad (1)$$

$$i_g(x) + w_g(x) + m_g(x) + h_g(x) = 1 \quad (2)$$

$$\frac{d}{dx}(L(x)w_l(x)) = -W J_w(x) \quad (3)$$

$$\frac{d}{dx}(L(x)m_l(x)) = -W J_m(x) \quad (4)$$

$$\frac{d}{dx}(L(x)h_l(x)) = -W J_h(x) \quad (5)$$

$$\frac{d}{dx}(G(x)w_g(x)) = -W J_w(x) \quad (6)$$

$$\frac{d}{dx}(G(x)m_g(x)) = -W J_m(x) \quad (7)$$

$$\frac{d}{dx}(G(x)h_g(x)) = -W J_h(x) \quad (8)$$

$$\frac{d}{dx}(G(x)i_g(x)) = 0 \quad (9)$$

where W ($= 300 \mu\text{m}$ for our chip) is the width of the liquid channel and $J_w(x)$, $J_m(x)$ and $J_h(x)$ are the molar fluxes (mol/s/m^2) of H₂O, MeOH and H₂O₂ across the membrane at position x , respectively. According to Bell *et al.*¹² and using the Raoult's equations, these fluxes can be expressed as follows:

$$J_w(x) = \frac{P_w}{H}(w_l(x)P_{\text{sat},w}(T) - w_g(x)P) \quad (10)$$

$$J_m(x) = \frac{P_m}{H}(m_l(x)P_{\text{sat},m}(T) - m_g(x)P) \quad (11)$$

$$J_h(x) = \frac{P_h}{H}(h_l(x)P_{\text{sat},h}(T) - h_g(x)P) \quad (12)$$

where H ($= 170 \mu\text{m}$ for our chip) is the thickness of the membrane, P ($= 500 \text{ mbar}$ in our experiments) is the pressure in the vapour channel and T is the temperature in the liquid channel. P_w , P_m and P_h are the permeability coefficients of liquid H₂O, MeOH and H₂O₂ across the membrane, respectively. According to Bell *et al.*¹², P_w and P_m , are at ambient temperature, close to $\text{Exp}(-25) \text{ mol/m}^2/\text{s/Pa}$. $P_{\text{sat},w}(T)$, $P_{\text{sat},m}(T)$ and $P_{\text{sat},h}(T)$ are the saturation pressures of H₂O, MeOH and H₂O₂, respectively. They are expressed as functions of T as follows:

$$P_{\text{sat},w}(T) = 101325 e^{13.7 - \frac{5120}{T+273.15}} \quad (13)$$

$$P_{\text{sat},m}(T) = 133 10^{8.8 - \frac{2002}{T+273.15}} \quad (14)$$

$$P_{\text{sat},h}(T) = e^{4.6+0.051 T} \quad (15)$$

where T is in $^{\circ}\text{C}$ and the pressures are in Pa. Equations (12) and (13) are given in *Lange's Handbook of Chemistry*,¹⁵ and equation (14) has been derived from data provided in a paper from J. J. van Laar¹⁶ and is valid for T between 50 and 100°C .

The molar flow rate of liquid introduced in the chip is written L_0 (mol/s). The molar fractions of H₂O, MeOH and H₂O₂ in this liquid are written w_0 , m_0 and h_0 , respectively. The following boundary conditions complete the balance equations:

$$L(0) = L_0, \quad m_l(0) = m_0, \quad h_l(0) = h_0, \quad (16)$$

$$G(L_p) = r L_0, \quad m_g(L_p) = \varepsilon, \quad h_g(L_p) = \varepsilon, \quad i_g(L_p) = 1-3\varepsilon \quad (17)$$

Equations (1-17) compose the mathematical model of the separation process. The introduction of an inert gas in the vapour channel at $x = L_p$ is considered in this model in order to avoid undetermined boundary conditions for $m_l(x)$ and $h_l(x)$ at $x = L_p$. After eliminating $i_g(x) = r L_0(1 - 3\varepsilon)/G(x)$ by solving (9) with (17), this model allows predicting the composition of the outlet phases ($w_l(L_p)$, $m_l(L_p)$, $h_l(L_p)$, $w_g(0)$, $m_g(0)$, $h_g(0)$) and the outlet fluxes ($L(L_p)$, $G(0)$), *i.e.* 8 unknowns, as functions of L_p , H , W , T , P , L_0 , w_0 , m_0 and h_0 . This algebraic-differential system of equations (1-8) is solved as a boundary-value problem using the continuation software AUTO-07p.²⁰ In order for the solutions to be compared with the experimental results, they are solved for $\varepsilon \rightarrow 0$ and $r \rightarrow 0$. In practice we have used $\varepsilon = 10^{-6}$ and $r = 10^{-3}$, for which the solutions were found to be independent on these parameters.

4. Results and discussion

Inoue *et al.*^{2,3} have produced from 3 wt% to 10 wt%² H₂O₂ solutions by direct synthesis from hydrogen (H₂) and oxygen (O₂) in a microfluidic device. This reaction was done in H₂O with the use of different catalysts (mostly palladium).

As mentioned previously, we foresee that next generation of direct synthesis of H₂O₂ in microfluidic chips will involve the use of MeOH as co-solvent. Three different liquid solutions are introduced in the chip, with different compositions: (i) $w_0 = 0.63$, $m_0 = 0.35$, $h_0 = 0.02$; (ii) $w_0 = 0.61$, $m_0 = 0.33$, $h_0 = 0.06$ and (iii) $w_0 = 0.15$, $m_0 = 0.74$, $h_0 = 0.11$. The chip is operated at different temperatures. These different compositions and temperatures are used to understand the effect of the operating conditions on the separation process efficiency. It can be calculated that the mass fraction of H₂O₂ in the liquid solutions introduced in the chip is between 3.3 and 12, covering thus the range of mass fractions produced by Inoue *et al.*² The experiments were repeated three times for each temperature and each inlet composition. In Fig. 2, the collected experimental data, *i.e.* molar fractions of H₂O₂, H₂O and MeOH,

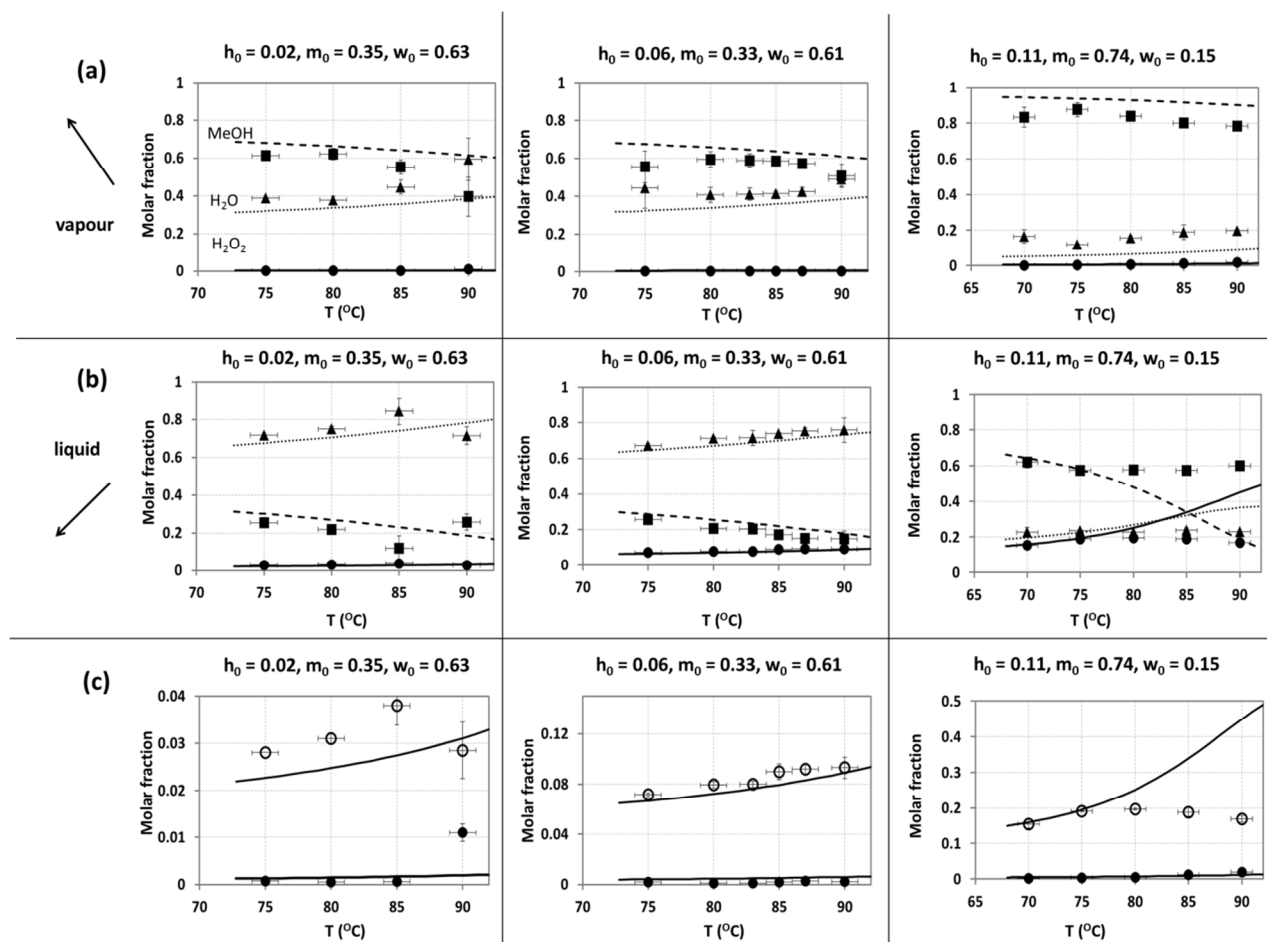


Fig. 2 Comparison of experimental results (symbols) and theoretical results (lines) for pervaporation of three different compositions of $\text{H}_2\text{O}_2/\text{H}_2\text{O}/\text{MeOH}$ mixtures at different temperatures. (a) outlet vapour phase, (b) outlet liquid phase, (c) H_2O_2 in vapour (black circles) and liquid phase (open circles) at the same graph. Squares and dashed lines: MeOH, triangles and dotted lines: H_2O , circles and solid lines: H_2O_2 .

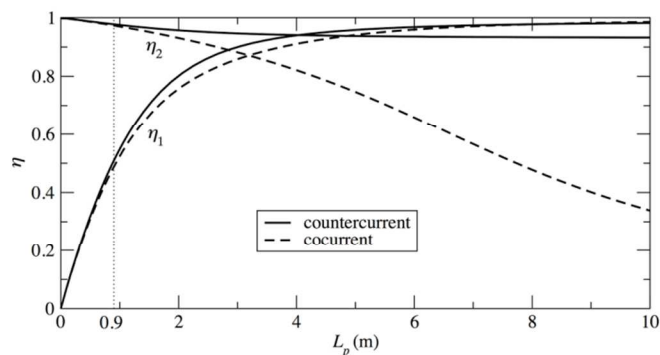
at the outlets of the chip, in the liquid and the vapour phases, are presented and compared to the model results (using values of P_w and P_m obtained in Bell *et al.*¹², at ambient temperature, and assuming $P_h = P_w$). It is important to mention here that, to use the model, the temperature T in the liquid channel has to be defined and there is an uncertainty on the experimental determination of T inside the channels for the reasons explained in the section 2.6.

After processing through the chip and for any of the liquid solutions used, H_2O_2 was concentrated and the MeOH concentration was decreased in the liquid phase. The experimental data presented in Fig. 2(b) shows that, at 85°C , the H_2O_2 concentration in the liquid phase is doubled namely from $h_0 = 0.02$ to $h_l(L_p) = 0.04$ and that the MeOH concentration in the liquid phase is decreased by a factor four from $m_0 = 0.35$ to $m_l(L_p) = 0.08$. Furthermore, only very small amounts (traces) of H_2O_2 are detectable in the vapour phase produced. It is an obvious consequence of the low volatility (compared to H_2O and MeOH) of H_2O_2 at the considered temperatures. The experimental results presented here thus demonstrate that the developed chip can be successfully operated to separate, to a certain extent, MeOH and H_2O_2 . The

maximum obtained concentration of H_2O_2 in the liquid outlet is close to 30 wt% (molar fraction of 0.2).

A mass balance realized on the experimental results highlights that, at high operating temperatures in the chip (above 85°C), the amount of H_2O_2 leaving the chip is significantly smaller than the amount of H_2O_2 entering the chip. This behaviour was expected as it is commonly known that an increase of the temperature favours the process of decomposition of H_2O_2 .¹⁷ Additionally, the liquid solutions introduced in the chip as well as the collected condensed vapours have a pH around 6, which is not optimum for the storage of H_2O_2 ; a pH below 5 is preferred.¹⁸ On the opposite, mass balances for experiments performed with temperature below 85°C highlight no significant decomposition of H_2O_2 . The vapour channel, which is the part of the device that is exposed to the highest temperature, is connected to vacuum. It highly decreases the time during which H_2O_2 is exposed to high temperature. This probably contributes to the very small H_2O_2 decomposition for $T < 85^\circ\text{C}$. For the above-mentioned reasons, a temperature of 85°C or lower should be used for the process of any $\text{H}_2\text{O}_2/\text{H}_2\text{O}/\text{MeOH}$ liquid solution in the chip. In our experiments we do not observe significant escape of MeOH

Fig. 3 Efficiencies of the chip as functions of L_p . Continuous line: chip operated with countercurrent flows, dashed lines: chip operated with co-current flows. $w_0 = 0.61$, $m_0 = 0.33$, $h_0 = 0.06$, $W = 300 \mu\text{m}$, $H = 170 \mu\text{m}$, $P = 500 \text{ mbar}$ and $T = 85$



°C. The dotted line indicates the outlet of the channel used in the experiments.

through the walls of the PDMS chip. This observation was verified by mass balances as detailed in Supp. Info. PDMS is permeable to gases but we expect that thanks to the applied negative pressure in the vapour channel and to the thick and highly cross-linked PDMS walls, escape of MeOH should be prevented.

We thus conclude that PDMS layers and PDMS membrane are compatible with the system used at all working temperatures.

When the collected outlet phases are characterized by NMR, no additional signal from the dissolution of PDMS by the used mixtures is detectable (see for example Fig. 1S in Supp. Info.). We also tested that no additional NMR signal was observed in a water solution of 50% H_2O_2 in which a piece of PDMS has been boiled for 1h. Pervaporation was also carried out in an analogical chip made of NOA 81 (Norland Optical Adhesives), which is known to be not permeable to gases, but when pervaporation is performed at high temperature unexpected additional NMR signals in NMR spectra are observed probably caused by the dissolution of NOA.

Although our PDMS microfluidic device with a PDMS membrane has a good compatibility with the processed solutions and shows no leakage issue, different materials can be used to make a chip with for instance the use of a selective membrane. Careful choice has to be made to prevent leakage which is often the problem for membranes in chips. In our case such a problem was not detected.

Yet, the geometry of the chip can still be investigated and improved. The use of segmented flow (by injecting nitrogen bubbles for instance) can improve the vapour transfer to the vapour channel which can result in decreasing the operating temperature and thus preventing the degradation of H_2O_2 .

A good agreement between the experimental data and the mathematical model is obtained except at high temperature (above 85°C). The discrepancies between the model and the experimental data are caused by different factors, which we discuss below.

First, as mentioned previously, there is an uncertainty on the values of T that have to be used in the model, for an adequate comparison with the experimental data.

Second, the decomposition of H_2O_2 at high temperature is not taken into account in the model. This contributes probably to the fact that the deviation between the experimental data and the model increases when the temperature inside the chip increases, and is typically larger than 85°C . This is clearly observed in Fig. 2.

Third, the expressions of $J_w(x)$, $J_m(x)$ and $J_h(x)$ are based on the use of the Raoult's equations. These equations are only valid for ideal solutions, which is not strictly our case.

Fourth, the values of P_w , P_m and P_h used for the simulations of the model were obtained by other authors (using an unspecified concentration of a curing agent) and are considered independent of the temperature. To increase the accuracy of the model, these permeability coefficients should be determined experimentally, at different temperatures, for the membrane used in this work. To conclude based on this analysis we foresee that the biggest discrepancy will be obtained at the highest temperature and for the solution containing the highest concentration of H_2O_2 . This solution is the furthest from ideal so the vapour pressure obtained using the Raoult's equations and used in our model will be the most different from the true vapour pressure.

Nevertheless, it is not our intention to provide a more complex description of the vapour-liquid equilibrium of the solutions to model the studied process, but rather to provide a simple model that allows grasping the general behaviour of the system and identifying the relevant key parameters. In that spirit, the correspondence between the model and the experimental data seems reasonable.

Yet, the model can be used to characterize qualitatively the operation of the chip. For this purpose, three efficiencies of the chip are defined:

$$\eta_1 = 1 - \frac{L(L_p)m_l(L_p)}{L_0m_0} \quad (18)$$

$$\eta_2 = \frac{L(L_p)h_l(L_p)}{L_0h_0} \quad (19)$$

$$\eta_3 = \eta_1 \eta_2 \quad (20)$$

The efficiency η_1 quantifies the transfer of the MeOH from the liquid channel to the vapour channel. The value of $\eta_1 = 1$ means that the MeOH introduced in the chip has been entirely transferred to the vapour channel. The efficiency η_2 quantifies the conservation of H_2O_2 in the liquid channel. The value of $\eta_2 = 1$ means that no H_2O_2 has been transferred in the vapour channel. The parameter η_3 can be seen as an overall efficiency of the chip that is equal to 1 only when η_1 and η_2 are equal to 1.

In order to avoid the decomposition of H_2O_2 , it is important to work at a maximum temperature of 85°C . If the objective of the operation of the chip is to remove almost the entire amount of methanol in the liquid phase ($\eta_1 \rightarrow 1$), the operating pressure of the chip should be selected such that even a pure methanol vapour phase leaving the chip could not be in equilibrium with the inlet liquid solution regarding the mass transfer of methanol

through the membrane ($J_m(0) > 0$). If this condition is fulfilled, any increase of the channels length L_p would lead to an increase of the amount of methanol transferred from the liquid to the vapour. According to Equation (11), this condition simply writes $m_0 P_{sat,m}(T) > P$. For $m_0 = 0.33$ (lowest considered value of m_0 in our experiments) and $T = 85$ °C, this condition is equivalent to $P < 712$ mbar, which is actually fulfilled in our setup. This highlights the importance of working at a reduced pressure, according to the composition of the liquid inlet.

Using the model, η_1 , η_2 and thus η_3 can be calculated as functions of L_p . For instance, for a liquid solution corresponding to the second set of our experiments ($w_0 = 0.61$, $m_0 = 0.33$, $h_0 = 0.06$), and for $W = 300$ μm , $H = 170$ μm , $P = 500$ mbar, $T = 85$ °C, η_1 and η_2 are presented, in Fig. 3, as functions of L_p . It can be seen that the performance of the chip can be strongly enhanced for longer channel. For instance, if $L_p = 4\text{m}$, $\eta_1 = \eta_2 = 0.94$, meaning that for the considered liquid solution, 94% of the MeOH introduced in the chip could be transferred to the vapour channel, while 94% of the H_2O_2 introduced in the chip would remain in the liquid channel.

The model can also be used to calculate the values of η_1 , η_2 and η_3 that would be obtained in a chip operated with a vapour outflow at $x = L_p$ (co-current flows) instead of at $x = 0$ (countercurrent flows). For this purpose, the minus signs appearing in Equations (6-8) have to be replaced by plus signs and the boundary conditions (17) have to be written at $x = 0$. Every other parameters of the system being the same, calculations show that the efficiencies obtained in the case of countercurrent flows are higher than the efficiencies obtained in the case of co-current flows. This is a consequence of the fact that, as it is well known in chemical engineering, countercurrent flows offer a higher average driving force for heat and mass transfers than co-current flows. Therefore, while in the case of Fig. 3 the overall efficiency η_3 is found, to continuously increase with L_p for the countercurrent flows up to 10m, it passes by a maximum at 3m for the co-current flows, where $\eta_3 = 0.75$. Beyond 3m, η_2 decreases quickly meaning that a large amount of H_2O_2 is then going to the vapour phase, reducing drastically the capacity of the chip to concentrate H_2O_2 in the case co-current flows.

5. Conclusions

We successfully designed and operated a chip for the pervaporation of $\text{H}_2\text{O}_2/\text{H}_2\text{O}/\text{MeOH}$ ternary mixtures in order to concentrate H_2O_2 by removing MeOH. Even if solutions with a low amount of H_2O_2 were considered up to now (the maximum obtained concentration of H_2O_2 in the liquid outlet is close to 30 wt%), this work can be seen as a proof of concept and is the first step towards the design of a purification chip meeting industrial requirements. We show that H_2O_2 can be successfully concentrated and MeOH removed to some extent already in a single chip. Technology and technical issues have been tackled and solutions described. Advantages and disadvantages of the chip have been discussed and further improvement proposed. A model of the chip has been developed and compared

successfully with experimental data. The discrepancies between the model and the experimental results are discussed. Such a model could allow, based on the composition of the liquid solution that should be processed, to design a chip to fulfil a given requirement.

The combined analysis of the experimental results and the model allows highlighting the key phenomena governing the operation of the chip. A significant thermal decomposition of H_2O_2 appears to happen at temperature above 85°C. Such temperature should thus be avoided. If the objective of the operation of the chip is to remove almost the entire amount of methanol in the liquid phase ($\eta_1 \rightarrow 1$), the operating pressure of the chip should be carefully selected such that even a pure methanol vapour phase leaving the chip could not be in equilibrium with the inlet liquid solution, regarding the mass transfer of methanol through the membrane. Using the model, it is also demonstrated that a chip with countercurrent vapour and liquid flows present higher efficiencies than a chip that would be operated with concurrent flows.

It is worth noticing that the developed model do not contain any unknown value. No fit is realized and the used values for the permeability are obtained from the literature.

To increase the accuracy of the model, the permeability coefficients of the membrane used in this work should be determined experimentally, at different temperatures. It would be also interesting to analyse the influence of the curing agent concentration on the membrane permeability coefficients.

Another interesting perspective of this work could be to compare the designed chip with a chip built with a porous membrane. Such a chip would be characterized by the presence of a vapour-liquid interface. Therefore, its operation might significantly differ from the one of the chip designed in this paper.

Finally, continuous purification of H_2O_2 in microdevices opens new perspectives of research, as it can be hazardous in batch processes.

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