INTERFACIAL TRANSPORT AND REACTIONS IN A MULTIPHASE MICROFLUIDIC SYSTEM

YALI ZHANG

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DISSERTATION

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Introduction

The broad ranges of functionality and versatility of microfluidic technology has promoted a large spectrum of applications in clinical chemistry, soil science, plant biology, biomedical science and so on [1–3]. Relying on the availability of rapid developing micro/nano-fabrication techniques, microdevices have transformed from addressing single processes, such as sampling, sample pretreatment, reaction, separation, detection and analysis, to integrated multi-step networks. Such integrated networks combined with fluidic controlling and detection components are known as "Lab on a Chip" (LoC) or "Micro-total-analysis-system" (μ TAS) [4–8].

The medium of interest among these applications frequently involves multiphase/aqueous-organic (A-O) fluids. Emulsions, for instance, play a decisive role in drug delivery [9], food processing [10], oil recovery [11], cosmetics [12] and hazardous material handling [13]. Within microdevices the reduced channel dimensions result in large interfacial area among such multiphase systems. Enhanced mixing and increased mass transfer across the interface can therefore be achieved. This significantly increases the process performance involving interfacial transport and reactions compare to these in the conventional macro-scale system. Flow segmentation can be completed within seconds [14], which normally requires tens of minutes in the macroscale system under the effect of gravity. Heterogeneous catalytic reactions (e.g. hydrogenation) involving gas-liquid-solid or liquid-solid systems can be effectively accelerated in such microscale system. The reduced diffusion length combined with strong velocity gradients (wall stress) enhance the process performance significantly. As such, controlling and exploiting the interface characteristic presents an ideal route to facilitate these interfacial transport phenomena.

In case of manipulating a multiphase system, understanding the governing forces can be insightful. In addition to interfacial forces acting on

fluids interfaces, multiphase system are influenced by gravity, inertia and viscous forces. This can be expressed by dimensionless numbers which compare the relative importance of different physical forces. The Bond number (Bo) compares gravity to interfacial tension and Weber number (We) compares inertia to interfacial tension.

$$Bo = \frac{\Delta\rho g d_h^2}{\sigma} \quad (1.1)$$

$$We = \frac{\rho U^2 d_h}{\sigma} \quad (1.2)$$

where $\Delta\rho$ is the density differences between the two phases, g is the acceleration of gravity, d_h is the characteristic channel dimension, σ is the interfacial tension and U represents a characteristic velocity. On the microscale, the downscaling of d_h results in a dramatically reduced $Bo \ll 1$. This manifests that the interfacial force dominates the gravitation force. Particularly, for aqueous-organic systems at ambient conditions without the presence of surfactants, the interfacial force exceeds gravity when d_h is narrower than 1 mm. The reducing of d_h to 1 μm makes the interfacial force six orders of magnitude larger than gravity [15]. Furthermore, in microfluidics, the typical flow velocity is less than or on the order of centimeters per second, corresponding to We numbers much smaller than unity. We can therefore expect to influence the behavior of multiphase systems by interface tuning.

In this thesis, we aim to exploit microfluidics by creating precisely-controlled interfaces. In case of immiscible aqueous-organic systems, we display methods to control their interfaces by tuning the interactions (**Chapter 2**). Channels with heterogeneous surface energies affect the dynamics of the droplet-based flows and facilitates the understanding of underlined physics (**Chapter 3**). In case of miscible aqueous-organic fluids, the large surface-to-volume ratio and enhanced mass transport is exploited by an integrated micro-separator/purificator to minimize the notorious concentration polarization phenomena (**Chapter 4**). In liquid-liquid parallel flow, the interface is stabilized by capillary forces providing an optimal platform to track the kinetics of interfacial reactions (**Chapter 5**).

1.1 Background

When a liquid contacts both a solid and a gas (or a solid and a second immiscible liquid), distinct configurations can be formed based on the corresponding interfacial energies (Fig. 1.1A). The liquid curvature is caused by the differences among interfacial tensions and can be represented by the contact angle θ . At equilibrium the force balance is described by Young's equation:

$$\sigma_{sg} = \sigma_{sl} + \sigma_{lg}\cos\theta \quad (1.3)$$

where σ is the interfacial tension between the respective phases, s , g , and l . In case of a water droplet with a contact angle $< 90^\circ$, the adhesive force is relative strong. Water tends to wet the solid surface. This surface is called hydrophilic. When the contact angle $> 90^\circ$, water droplet tends to roll up and reduce the contact area. This is called a hydrophobic surface. Bringing water to a corresponding microchannel, concave and convex interfaces will result (Fig. 1.1B).

Figure 1.1: (A) The forces acting at a triple interface for a liquid droplet on a flat solid surface. (B) Liquid droplet in the corresponding microchannel.

When an interface is curved, the pressures on the two sides of the surface are different. The interfacial forces are balanced by the pressure difference and can be described by Laplace equation:

$$\Delta p = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (1.4)$$

where R_1 and R_2 are describing the radii of curvature of the interface. Controlling the curvature and hence the pressure difference is an effective way to manipulate multiphase fluids on the microscale. As the interfacial

forces are dominant on the microscale, the Capillary number (Ca) become a very useful dimensionless number to describe the flow phenomena.

$$Ca = \mu U / \sigma \quad (1.5)$$

where μ (Pa·s) is the dynamic viscosity of the continuous phase. The Capillary number Ca measures the ratio of viscous and interfacial forces. It is controlled by the properties of the channel (surface energy) and fluid (viscosity and velocity), but is irrelevant to the channel dimensions. It can be adopted to describe multiphase flow phenomena on the microscale, such as flow formation [16], sizing [17], coalescing [18], mixing [19] and splitting [20].

1.1.1 Droplet formation

Microsystems provide excellent control regarding manipulation of individual droplets and dynamics allowing us to understand the underlying physics of emulsions [21, 22]. Well-defined emulsions can be produced using microfluidic devices such as co-flowing [23], T- and Y-junctions [24], and flow focusing structure [25, 26] (Fig. 1.2A). In T- or Y-junctions, droplets of the disperse phase are generated as a result of the shear and interfacial forces. Flow-focusing configurations facilitate droplet formation in terms of generating small and highly viscous droplets. In this configuration, the disperse phase is injected through a central channel into a narrow orifice while the continuous phase is injected through two outside channels [27].

Zheng and co-workers have investigated the dependence of the droplets formation on Ca and water fraction (wf) by introducing two aqueous streams to a carrier liquid in a cross configuration. Four flow regimes were observed as illustrated in Fig. 1.2B. For very small Ca , (~ 0.004), large droplet-based flow is observed along the channel. For increasing Ca alternating droplet formation is found with decreased droplet size. When $Ca > 0.15$, parallel laminar flow is obtained at a water fraction of 0.2. Still, such parallel flows are unstable and break up into droplets further downstream. The authors used this technique to index the droplets composition for protein crystallization.

The droplet shape and segmentation is a direct consequence of the

affinity of both fluid phases with the channel wall. By employing a surface modified in dissimilar wettability is therefore of interest in altering the emulsion dynamics. Shui et al observed emulsion inversion using a microchannel with adjacent hydrophobic and hydrophilic segments [29]. Chen [28] performed experiments by controlling adhesion of droplets by changing Ca using a capillary with a similar design (Fig1.2(C)). He found a critical Ca for adhesion, correlated to the capillary dimension (d) and formed droplet size (D), $Ca \sim D^{3/4}/d^{3/2}$. Both of the studies demonstrate that this technique finds promising industry applications, such as in food processing and oil recycling (Fig. 1.2(C)).

Figure 1.2: (A) Different configurations for emulsion formation. (B) Dependency of flow patterns on capillary number Ca . (a) Schematic illustration of the experimental setup. (b-k) Flow patterns at different Ca and wf . (C) Emulsion in a capillary with selectively modified wettability [16]. (a) Droplets adhere to the capillary wall after passing from a hydrophilic to a hydrophobic segment. (b) Demonstration of droplet adhesion for the recycling of oil from water [28].

1.1.2 Surface modification

Surface hydrophobization is an effective method to manipulate fluid patterns in confining channels by modulating interfacial energies between

fluids and channel walls, such as controlling G-L, parallel L-L interfaces and emulsions of water-in-oil (W/O) or oil-in-water (O/W) [29–32]. The presence of silanol groups on glass surfaces allow covalent grafting of self-assembled monolayers (SAMs) to affect the surface energy. This approach has been widely used for chemical surface modification using alkanesilanes on glass. The generated new surface shows high mechanical and chemical robustness with very few defects [33, 34]. Microchannels can be hydrophobized via both a homogeneous modification and a selective modification process. The homogeneous hydrophobized channel wall is relative simple to obtain. For a spatial selective hydrophobization, the channel can be partial modified via co-flowing streams that define the surface grafting process [35]. Other strategies, that rely on lithography, can be envisioned to laterally control the surface characteristics.

1.1.3 Interfacial transport

Concentration polarization

Mass transport across an interface can establish enriched or depleted zones near this interface. This phenomena is called concentration polarization and its effects can be particularly notorious in the fields of electrochemistry and membrane separations. Figure 1.5 illustrates the formation of concentration gradients on both sides of a dense membrane contacting liquid and gas in a pervaporation process. The mass transfer resistances in the membrane ($1/k_m$) and the liquid phase flowing adjacent to the membrane surface ($1/k_l$) determines the flux of the migrating specie. The resistance of the gas phase can normally be neglected due to the fast transport in the gas phase. In conventional scale, the mass transport limiting region lies in the liquid phase adjacent to the membrane surfaces, named depletion zone or liquid boundary layer.

The Peclet number, Pe , is normally selected to indicate the significance of concentration polarization. This dimensionless number describes the relative importance of diffusion and convection in the liquid boundary layer and is defined as

$$Pe = Uh/D \quad (1.6)$$

where U is the permeation velocity, h is the characteristic thickness of the boundary layer, and D is the diffusion coefficient of the migrating components of interest. When $Pe > 1$, the convective transport in the

Figure 1.3: Schematic drawing of concentration polarization in a co-flow pervaporation system

flow direction is more efficient than that of diffusive transport towards the membrane. Large concentration gradient occurs perpendicularly to the membrane and the concentration polarization is significant. When $Pe < 1$, the diffusive transport is fast compare to the permeation flux through the membrane and a reduced thickness of the depletion zone is achieved. The associated concentration polarization is insignificant. However, for processes involving the selective removal of a minority component, the concentration polarization can already be very significant even at lower Pe numbers [36].

Membrane integrated micro-separators

Transport phenomena are of great importance for membrane separation process performance. The mass transport across the membrane interface between parallel flows is governed by the molecular diffusion. The reduced diffusion length, channel width (W), results in a shorter diffusion time ($t = W^2 D^{-1}$). A decrease in width of the channel by a factor 10 leads to a decrease in the diffusion time of a factor 100. This confirms the high potential efficiency for micro-separators. In case of miscible aqueous-organic flows, integrating membrane technology into microfluidic devices presents an ideal strategy for effective separations. Various membrane processes, such as pervaporation [37, 38], nanofiltration [39, 40], membrane distillation [41] and desalination [42] have been performed inside microsystems ranging from proof-of-concept studies to real applications in terms of pre-filtration, separation and reaction [43].

In particular, pervaporation is a promising membrane process capable of removing miscible organic solvents from aqueous feeds. The process is performed by bringing a liquid mixture in contact with a membrane while a vacuum or a sweeping gas is applied to the other side. Species with higher affinities for the membrane, diffuse preferentially through the membrane and vaporise at the other side of the membrane. The created concentration gradient or the partial pressure difference across the membrane is the driving force for the separation process. In conventional scale, this process suffers from concentration polarization due to depletion of the minor component at the liquid-membrane surface, already at relatively low Pe numbers [36].

Various direct and indirect experimental techniques have been employed to quantify the mass transfer resistance of the membrane and the liquid boundary layer by employing the 'resistance-in-series' model. For example, the overall resistance ($1/k_{ov}$) can be experimentally determined using a Wilson plot [44], as indicated in Fig. 1.4. Particularly for relatively thick homogeneous membranes with a low permeability for the organic component, $1/k_m$ is supposed to be proportional to the membrane thickness. By plotting the $1/k_{ov}$ as a function of the membrane thickness, a straight line is obtained. The intercept is the $1/k_l$ and the slope is equal to the reciprocal value of the membrane permeability. This method is evidently somewhat cumbersome, as it requires permeation experiments done with a series of membranes of different thickness.

Figure 1.4: Mass transfer resistance as a function of membrane thickness

The influence of hydrodynamics on the liquid boundary can also be obtained more directly. k_l varies along the flow direction since the depletion of the solute through the membrane expands the boundary layer thickness. The averaged k_l is employed to describe the mass transport efficiency in

the liquid boundary by implementing semi-empirical correlations [45]. As presented in Eq 1.3 the Sherwood number (Sh) yields the average k_l as a function of feed flow rate and the dimensions of the configuration.

$$Sh = \frac{k_l d}{D} = c + a(Re \cdot Sc(\frac{d}{l}))^b \quad (1.7)$$

where Re is the Reynolds number, Sc is the Schmidt number, d is the hydraulic diameter of the configuration, D is the mass transfer coefficient of the specie and a , b , c are constants and the values vary with the difference in configurations and flow patterns. In a straight channel with laminar flow ($Re < 2000$), the Graetz-Lvque equation can be applied to obtain the constant values [46]. In a developing concentration profile, Sh varies with the flow rate and module configuration while in a fully developed concentration profile, Sh becomes constant as the thickness of the depletion zone (δ_l) does not grow any further.

1.1.4 Interfacial reactions

The effective interfacial transport within microfluidic systems also present advantages in conducting and investigating interfacial reactions. The well-controlled laminar flow pattern enables a precise definition of the reaction contact time, shape and size of the interface [5, 47].

Performing interfacial reactions in microsystems has two objectives. Firstly, the interfacial reaction can be employed for a broad range of microproductions. Examples like polymer particles, inorganic particles, nanoparticles or microgel preparation using droplet-based flow [22]. The reaction at a liquid-liquid interface can again be categorized according to the Pe number. For laminar flow at small Peclet number, diffusion is the driving force for the reaction. Such process are used to fabricate microelectrodes [48] and polymer membranes using interfacial polymerization [49]. For laminar flow at high Peclet numbers, convective transport is dominant. Such a flow condition is optimal for 'sheathing' one fluid with another. The monomer in one phase can be photopolymerized 'on the fly' at the exit of the microfluidic device [50]. This method allows continuous generation of microscopic fibers and tubes and provides insight into the polymer growth process.

In the second case, the use of well-defined interfaces enables kinetic

studies of reactions at millisecond time scales along with process characterization [51]. Examples include the in-situ characterization of interfacial polymerization process for the production of micro-capsules [52] and the lactone cleavage rate constants at the toluene/water and heptane/water interface [53].

Basics of interfacial polymerization

Interfacial polymerization occurs at an interface between an aqueous solution containing a monomer and an organic solution containing a second monomer. The polymerization of the two reactants starts at the initial liquid-liquid interface. The increase in thickness and density of the film that is forming hinders the diffusion of unreacted monomers, forcing the polymerization reaction to be self-limiting. The formed film can exhibit excellent salt retention and is typically employed in preparation of thin film composite (TFC) membranes or encapsulations. Applications of TFC membranes include purification and desalination of water, liquid separation and waste treatment. Such membranes are fabricated by first loading an aqueous solution of difunctional amines in a flat-sheet support which is then brought into contact with an organic phase containing the trifunctional acid chlorides. By tuning the chemistry formula, a sub-10 nm thick IP membrane can be fabricated with certain mechanical stability [54]. The membrane formed on an alumina support exhibits an extraordinary solvent permeability, which is more than two orders of magnitude higher than that of the commercial membrane. Understanding the reaction mechanism of IP processes is of great importance to guide the selection of chemistry and optimize the resulting membrane performance.

Significant work has been performed to correlate the formation kinetics to the film properties, in particular to the molecular separation performance [9, 55–57, 59]. However, the understanding of the formation kinetics of IP films is limited due to the extremely rapid kinetics and lack of in-situ analysis techniques. This has led to intensive computational work to explore the film formation kinetics. Figure 1.5 illustrates the development of the formation kinetics based on simulations. The latest developed model demonstrates four stages during the film formation process. First, an incipient film is formed ($\delta \sim t^2$), followed by a diffusion limited growth stage ($\delta \sim t^{1/2}$), to a film densifying stage ($\delta \sim t^{1/3}$), ending in a fully diffusion limited film growth ($\delta \sim t^0$). These models are referred to as ‘double-layer models’, as the film formed by this multi-stage process consists of a selective dense layer atop a more loose layer.

Figure 1.5: A schematic representation of the film thickness dependence on reaction time as proposed by Enkelmann and Wegner in 1976 [57] and the current accepted multiple stage model proposed in 2009 by Oizerovich-Honig et.al [59].

1.2 Scope of the thesis

Within the scope of this thesis, interfacial reaction and transport phenomena and their applications in microfluidic configurations are investigated.

In **Chapter 2**, two distinct processes for selective hydrophobization inside microchannels are presented. First, we explored the feasibility of applying silicon oil in a glass microchannel for selective hydrophobization using the protocol described by Arayanarakool [60]. Contributions of various experimental parameters on the resulting grafting efficiency are investigated. Second, an alternative approach for spatial patterning wettability inside a micro-capillary tube is presented. The method combines photolithography with SAM chemistry and allows patterning alternative hydrophobic/hydrophilic segments inside a capillary.

In **Chapter 3**, a capillary modified with heterogeneous surface wettability is employed to investigate its influence on emulsion dynamics. The oil-in-water emulsions were generated in a cylindrical glass capillary with a desired hydrophobic segment in the middle. The dynamics of the formed droplets in terms of morphology and motion are characterized by controlling the flow rates of both water and oil streams using a chemically heterogeneous wall.

In **Chapter 4**, the concept of pervaporation is implemented into microfluidic devices to investigate the mass transport limitations. The mass transport resistances at liquid boundary layer and membrane are

investigated both experimentally and numerically. A performance study was conducted to improve the system efficiency and further optimize the configuration design.

In **Chapter 5** presents the studies on interfacial reactions via stabilized liquid-liquid interfaces in microfluidic channels. Free-standing films are formed by interfacial polymerization using different chemistries to provides insight in the reaction kinetics. The microfluidic devices allow a direct visualization and characterization of the film formation process.

In **Chapter 6**, a summary of the microfluidic studies is presented. It gives concluding remarks on the obtained results and recommendations for future work.

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Bibliography

- [1] Nguyen NT, Wereley ST (2002) *Fundamentals and applications of microfluidics* (Artech House).
- [2] Whitesides GM (2006) The origins and the future of microfluidics. *Nature* 442:368–373.
- [3] Stone HA, Kim S (2001) Microfluidics: basic issues, applications, and challenges. *AIChE J* 47:1250–1254.
- [4] Thorsen T, Maerkl SJ, Quake SR (2002) Microfluidic large-scale integration. *Science* 298:580–584.
- [5] Hartman RL, Jensen KF (2009) Microchemical systems for continuous-flow synthesis. *Lab chip* 9:2495–2507.
- [6] Broyles BS, Jacobson SC, Ramsey JM (2003) Sample filtration, concentration, and separation integrated on microfluidic devices. *Anal Chem* 75:2761–2767.
- [7] Webb D, Jamison TF (2010) Continuous flow multi-step organic synthesis. *Chem Sci* 1:675.
- [8] Mark D, Haeberle S, Roth G, von Stetten F, Zengerle R (2010) Microfluidic lab-on-a-chip platforms: requirements, characteristics and applications. *Chem Soc Rev* 39:1153–1182.
- [9] Vasiljevic D, Parojcic J, Primorac M, Vuleta G (2006) An investigation into the characteristics and drug release properties of multiple w/o/w emulsion systems containing low concentration of lipophilic polymeric emulsifier. *Int J Pharm* 309:171–177.

- [10] Leal-Calderon F, Thivilliers F, Schmitt V (2007) Structured emulsions. *Curr Opin Colloid Interface Sci* 12:206–212.
- [11] Huang JS, Varadaraj R (1996) Colloid and interface science in the oil industry. *Curr Opin Colloid Interface Sci* 1:535–539.
- [12] Yoshida K, Sekine T, Matsuzaki F, Yanaki T, Yamaguchi M (1999) Stability of vitamin a in oil-in-water-in-oil-type multiple emulsions. *J Am Oil Chem Soc* 76:1–6.
- [13] Ouyang Y, Mansell R, Rhue R (1995) Emulsion-mediated transport of nonaqueous-phase liquid in porous media: A review. *Crit Rev Env Sci Technol* :269–290.
- [14] Hibara A, et al. (2002) Stabilization of liquid interface and control of two-phase confluence and separation in glass microchips by utilizing octadecylsilane modification of microchannels. *Anal Chem* 74:1724–1728.
- [15] Günther A, Jensen KF (2006) Multiphase microfluidics: from flow characteristics to chemical and materials synthesis. *Lab Chip* 6:1487–1503.
- [16] Zheng B, Tice JD, Ismagilov RF (2004) Formation of droplets of alternating composition in microfluidic channels and applications to indexing of concentrations in droplet-based assays. *Anal Chem* 76:4977–4982.
- [17] Dendukuri D, Tsoi K, Hatton TA, Doyle PS (2005) Controlled synthesis of nonspherical microparticles using microfluidics. *Langmuir* 21:2113–2116.
- [18] Zheng B, Ismagilov RF (2005) A microfluidic approach for screening submicroliter volumes against multiple reagents by using preformed arrays of nanoliter plugs in a three-phase liquid/liquid/gas flow. *Angew Chem Int Ed* 44:2520–2523.
- [19] Shestopalov I, Tice JD, Ismagilov RF (2004) Multi-step synthesis of nanoparticles performed on millisecond time scale in a microfluidic droplet-based system. *Lab Chip* 4:316–321.
- [20] Link D, Anna SL, Weitz D, Stone H (2004) Geometrically mediated breakup of drops in microfluidic devices. *Phys Rev Lett* 92:054503.

-
- [21] Baroud CN, Gallaire F, Dangla R (2010) Dynamics of microfluidic droplets. *Lab Chip* 10:2032–2045.
 - [22] Seemann R, Brinkmann M, Pfohl T, Herminghaus S (2012) Droplet based microfluidics. *Rep Prog Phys* 75:016601.
 - [23] Shah RK, et al. (2008) Designer emulsions using microfluidics. *Mater Today* 11:18–27.
 - [24] Nisisako T, Torii T (2008) Microfluidic large-scale integration on a chip for mass production of monodisperse droplets and particles. *Lab Chip* 8:287–293.
 - [25] Anna SL, Bontoux N, Stone HA (2003) Formation of dispersions using “flow focusing” in microchannels. *Applied physics letters* 82:364–366.
 - [26] Ward T, Faivre M, Abkarian M, Stone Ha (2005) Microfluidic flow focusing: Drop size and scaling in pressure versus flow-rate-driven pumping. *Electrophoresis* 26:3716–3724.
 - [27] Takeuchi S, Garstecki P, Weibel DB, Whitesides GM (2005) An axisymmetric flow-focusing microfluidic device. *Adv Mater* 17:1067–1072.
 - [28] Chen H, Dong E, Li J, Stone HA (2013) Adhesion of moving droplets in microchannels. *Appl Phys Lett* 103:131605.
 - [29] Shui L, van den Berg A, Eijkel JC (2009) Interfacial tension controlled w/o and o/w 2-phase flows in microchannel. *Lab Chip* 9:795–801.
 - [30] Lam KF, Sorensen E, Gavriilidis A (2013) Review on gas–liquid separations in microchannel devices. *Chem Eng Res Des* 91:1941–1953.
 - [31] Atencia J, Beebe DJ (2005) Controlled microfluidic interfaces. *Nature* 437:648–655.
 - [32] Shui L, Eijkel JC, van den Berg A (2007) Multiphase flow in microfluidic systems—control and applications of droplets and interfaces. *Adv Colloid Interface Sci* 133:35–49.
 - [33] Gooding JJ, Mearns F, Yang W, Liu J (2003) Self-assembled monolayers into the 21st century: recent advances and applications. *Electroanalysis* 15:81–96.

- [34] Schreiber F (2000) Structure and growth of self-assembling monolayers. *Prog Surf Sci* 65:151–257.
- [35] Zhao B, Moore JS, Beebe DJ (2001) Surface-directed liquid flow inside microchannels. *Science* 291:1023–1026.
- [36] Wijmans J, et al. (1996) The role of boundary layers in the removal of volatile organic compounds from water by pervaporation. *J Membr Sci* 109:135–146.
- [37] Leng J, Joanicot M, Ajdari A (2007) Microfluidic exploration of the phase diagram of a surfactant/water binary system. *Langmuir* 23:2315–2317.
- [38] Ziemecka I, Haut B, Scheid B (2015) Hydrogen peroxide concentration by pervaporation of a ternary liquid solution in microfluidics. *Lab Chip* 15:504–511.
- [39] Kaufman Y, Kasher R, Lammertink RG, Freger V (2012) Microfluidic nf/ro separation: Cell design, performance and application. *J Membr Sci* 396:67–73.
- [40] Kolfschoten RC, Janssen AE, Boom RM (2011) Mass diffusion-based separation of sugars in a microfluidic contactor with nanofiltration membranes. *J Sep Sci* 34:1338–1346.
- [41] Hartman RL, Naber JR, Buchwald SL, Jensen KF (2010) Multistep microchemical synthesis enabled by microfluidic distillation. *Angew Chem Int Ed* 49:899–903.
- [42] Roelofs SH, van den Berg A, Odijk M (2015) Microfluidic desalination techniques and their potential applications. *Lab Chip* 15:3428–3438.
- [43] De Jong J, Lammertink R, Wessling M (2006) Membranes and microfluidics: a review. *Lab Chip* 6:1125–1139.
- [44] McCarthy M, Molloy N (1974) Review of stability of liquid jets and the influence of nozzle design. *Chem Eng J* 7:1–20.
- [45] Matthiasson E, Sivik B (1980) Concentration polarization and fouling. *Desalination* 35:59–103.
- [46] Nijhuis HH (1990) *Removal of trace organics from water by pervaporation: a technical and economic analysis* (University of Twente).

- [47] Doku GN, Verboom W, Reinhoudt DN, Van Den Berg A (2005) On-microchip multiphase chemistry—a review of microreactor design principles and reagent contacting modes. *Tetrahedron* 61:2733–2742.
- [48] Kenis PJ, Ismagilov RF, Whitesides GM (1999) Microfabrication inside capillaries using multiphase laminar flow patterning. *Science* 285:83–85.
- [49] Zhao B, Viernes NO, Moore JS, Beebe DJ (2002) Control and applications of immiscible liquids in microchannels. *J Am Chem Soc* 124:5284–5285.
- [50] Jeong W, et al. (2004) Hydrodynamic microfabrication via “on the fly” photopolymerization of microscale fibers and tubes. *Lab Chip* 4:576–580.
- [51] Gerdts CJ, Sharoyan DE, Ismagilov RF (2004) A synthetic reaction network: chemical amplification using nonequilibrium autocatalytic reactions coupled in time. *J Am Chem Soc* 126:6327–6331.
- [52] Quevedo E, Steinbacher J, McQuade DT (2005) Interfacial polymerization within a simplified microfluidic device: capturing capsules. *J Am Chem Soc* 127:10498–10499.
- [53] Tokimoto T, Tsukahara S, Watarai H (2005) Lactone cleavage reaction kinetics of rhodamine dye at liquid/liquid interfaces studied by micro-two-phase sheath flow/two-photon excitation fluorescence microscopy. *Langmuir* 21:1299–1304.
- [54] Karan S, Jiang Z, Livingston AG (2015) Sub-10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation. *Science* 348:1347–1351.
- [55] Jegal J, Min SG, Lee KH (2002) Factors affecting the interfacial polymerization of polyamide active layers for the formation of polyamide composite membranes. *J Appl Polym Sci* 86:2781–2787.
- [56] Morgan PW, Kwolek SL (1959) Interfacial Polycondensation. 11. Fundamentals of Polymer Formation. *J Poly Sci* XL:299–327.
- [57] V Enkelmann GW (1976) Mechanism of Interfacial Polycondensation and the Direct Synthesis of Stable Polyamide Membranes. *Makromol Chem* 177:3177–3189.

- [58] Kim C, Kim J, Roh I, Kim J (2000) The changes of membrane performance with polyamide molecular structure in the reverse osmosis process. *J Membr Sci* 165:189–199.
- [59] Veríssimo S, Peinemann KV, Bordado J (2006) Influence of the diamine structure on the nanofiltration performance, surface morphology and surface charge of the composite polyamide membranes. *J Membr Sci* 279:266–275.
- [60] Arayanarakool R, Shui L, van den Berg A, Eijkel JC (2011) A new method of uv-patternable hydrophobization of micro-and nanofluidic networks. *Lab Chip* 11:4260–4266.

Selective Surface Modification in an Enclosed Microchannel

SUBSTRATE functionalization is of great importance in successfully manipulating flows and liquid interfaces in microfluidic devices. Herein, we have explored the mechanism of hydrophobization using silicon oil on glass substrates and propose an alternative approach for spatial patterning of surface energy in a micro-capillary tube. A faster reaction rate and higher contact angle are obtained when the operating temperature is ≥ 60 °C, compared to that by UV irradiation process. Such findings provide a simple hydrophobization process in micro- and nanochannels compared to the UV and plasma combined process. Due to the long reaction time and heat generation by UV irradiation, silicon oil is an inappropriate material to pattern a glass surface with dissimilar wettability. The method of patterning wettability combines a tailored-photolithography process with self-assembled monolayer formation. The modified micro-capillaries shows very sharp boundaries between the alternating hydrophilic/hydrophobic segments with an achieved smallest dimension down to 60 micrometer. Our two-step method makes this technique versatile allowing to pattern multiple types of functional groups in discontinuous structures in an enclosed channel.

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2.1 Introduction

In microfluidic systems, substrate functionalization plays a key role in manipulating interfacial transport as a result of high surface area to volume ratio. Hydrophobizing a surface effectively manipulates the fluid patterns by means of modulating interfacial forces between fluids and channel walls, such as controlling gas-liquid, parallel liquid-liquid interfaces and determining the types of emulsions in terms of water-in-oil (W/O) or oil-in-water (O/W) [1–4]. The use of glass for microchip fabrication has tremendous advantages due to its excellent optical transparency, tunable surface properties and high resistance to mechanical stress, organic chemicals and high temperatures.

Self-assembled monolayers (SAMs) have been widely used for chemical surface modification e.g. by using alkanethiols on gold or alkanesilanes on glass. Such chemicals form covalent bonds or networks to the surface that generates new surface functions with high mechanical and chemical robustness and very few defects [5–7]. Alkanesilanes are often employed to react with hydroxyl groups on glass or silicon substrates. The modification process is rapid and can be performed via both solution and vapor depositions. Problems arise when applying the SAM chemistry inside microfluidic networks. The organosilanes are highly reactive to water which results in aggregation. The formed particulate debris can devastate the fluidic application in terms of channel blocking and contaminations. For these reasons, meticulous dehydrating and post-cleaning processes are required when applying SAMs chemistry within microfluidics.

Selectively tuning of surface wettability facilitates new applications for microsystems and promotes fundamental understanding, for example in manipulating droplets [2, 3], creating hydrophobic vales [8, 9], solvent extraction of metal ions or organics [10, 11] and attaching biomaterials [12–15]. Patterning dissimilar surface chemistries on flat substrates is prevalently accomplished using techniques such as micro-contact printing, electrochemical deposition, and SAMs formation combined with photomasks [16–19]. However, the techniques of modifying surfaces in an enclosed microchannel are often complicated and have their limitations. Using a soft photolithography process requires post bonding procedures [13, 20, 21]. Heat induced patterning by particles [22] causes significant thickness difference ($> \mu\text{m}$) between the hydrophilic and hydrophobic regions. Electrochemical deposition [23] often applied to microchip based systems, requires

complex chip design and implemented electrodes. Vong [24] has fabricated dissimilar wettability in a microchannel by using local photochemical reaction with a tailored linker in a complex route. Photochemical patterning is also possible by decomposing the coated monolayers under UV irradiation. Such a method is clean but normally restricted to certain materials and chemistries [21]. Besides, the resulting hydrophilic region may turn hydrophobic after several days [25]. Flow controlled surface modification is capable of fabricating defined heterogeneous wettability in a microchannel but is restricted to the flow direction [26].

Although a versatile method for selective hydrophobization in microfluidics is desired, current methods are limiting. In this work, we have attempted two distinct processes to modify surfaces inside microdevices. In this first section, we have explored the feasibility of applying silicon oil in a glass microchannel for selective hydrophobization using the protocol described by Arayanarakool [27]. Subsequently, we propose an alternative approach for spatial patterning wettability inside a micro-capillary tube by coupling photolithography with SAM chemistry. The fabrication processes and results of these two methods are illustrated in detail in the following sections.

2.2 Experimental

2.2.1 Materials

Silicon oil (20 cSt, Sigma-Aldrich), Quartz and borofloat glass microcapillary tubes (TCO workshop, University of Twente) were used with 1.5 mm O.D. and 0.98 mm I.D., respectively. Potassium hydroxide (99 % Sigma-Aldrich), positive photoresist (Olin Oir 907-35, Arch Chemicals, Inc), Nitric acid (99 % Sigma-Aldrich), Perfluorodecyltrichlorosilane (FDTS, 97%, Sigma-Aldrich), HFE-7500 (Fluorochem), Chlorotrimethylsilane (CTMS, 97%, Sigma-Aldrich), n-Octyltriethoxysilane (OTES, 98%, Sigma-Aldrich), Hexane (>97.0%, Sigma-Aldrich), Ethanol (> 99.8%, Sigma-Aldrich), and Acetone (> 99.9%, Sigma-Aldrich) were used as received.

2.2.2 Hydrophobization by silicon oil

Prior to use, all the diced glass slides (2x2 cm x cm) were firstly cleaned by immersing in nitric acid for 30 min and rinsed by DI water. Dehydration was followed by baking the cleaned slides in oven at 120 °C for overnight with a nitrogen flow.

UV induced hydrophobization The cleaned slides were immersed in silicon oil in a glass petri-dish and placed in an enclosed UV box with a wavelength of 264 nm. The irradiating time was varied from 30, 60, 90 to 120 min. The temperature raising along the irradiate time in the UV box was measured and recorded on-line by a thermo couple (National instruments, NI USB-TC01). Samples were prepared in two groups, with and without oxygen plasma pre-treatment.

Thermal induced hydrophobization The cleaned glass slides were immersed in silicon oil in a glass petri-dish and placed in an oven. The performed temperatures were 60, 80 °C with reaction time from 30, 60, 90 to 120 min. Samples were prepared in two groups, with and without plasma.

After the modification, all the modified glass slides were cleaned by immersing in n-hexane (> 97.0%, Sigma-Aldrich), acetone (> 99.9%, Sigma-Aldrich) and isopropanol (> 99.9%, Sigma-Aldrich). The cleaned slides were dried in a nitrogen box for 1 day. Both static and dynamic contact angle measurements on the glass slides were performed using DI water (Dataphysics, OCA20, Germany). The average contact angle with standard deviations were calculated.

2.2.3 Positional patterning inside microchannels

The micro-capillary tube was cleaned meticulously to strengthen the adhesion of the photoresist (PR) to the glass surface. The capillary was first filled with a Tetramethylammonium hydroxide (TMAH, 25 v/v %) solution for 1 min and then placed in DI water and sonicated for 10 min. After this it was rinsed in DI water to remove any remaining TMAH and immersed in nitric acid for 10 min. The cleaned capillary was rinsed again by DI water and dried on a hotplate at 120 °C. The dried capillary was filled with positive PR solution using a syringe and spin-coated at 4000 rpm for 30 sec, leaving a dense and uniform PR layer on the inner wall.

The coated capillary was pre-baked in a vacuum oven kept at a pressure of 2 mbar with a nitrogen flow at 70 °C for 1 h to evaporate the solvents and strengthen the PR layer adhesion onto the inner surface. The capillary was horizontally placed under an optical mask for UV exposure (12 mW/cm²) for 20 s. The length of the hydrophobic segments was designed as 6, 60, 600 and 6000 μ m, equal to the corresponding hydrophilic segments. The developing solution was introduced into the capillary by a gentle syringe flow to dissolve the exposed PR layers (targeted hydrophobic segment) for 1 min and the capillary was rinsed by DI water after that. The capillary was placed on a hotplate at 150 °C to remove any surface water from the capillary.

A Perfluorodecyltrichlorosilane (FDTS) /HFE-7500 (0.4 v/v) solution was pumped through the capillary at 1 mL min⁻¹ for 1 h to hydrophobize the exposed regions. At last, the capillary was cleaned by hexane to flush out the unreacted FDTS and by a acetone/iso-propanol solution to dissolve the patterned PR layers.

2.2.4 Characterization

Contact angle measurements Both static and dynamic contact angle measurements on the modified substrates were performed using a Data-physics System (Dataphysics, OCA20, Germany). The sessile drop mode was used to determine the static contact angle and sessile needle-in mode was used for the dynamic contact angle. The results are averaged over 3 measurements on each sample.

Atomic force microscopy The topographic and height profiles of a modified flat glass sample were characterized by atomic force microscopy (AFM, Veeco Dimension Icon with ScanAsyst) at room temperature. The AFM was operated in tapping mode using Si cantilevers (MikroMasch) with resonance frequencies from 65 to 130 KHz and spring constant from 0.6-2 N/m. AFM images of 512 $\times$ 512 pixels were obtained for sample surfaces and the roughness was evaluated via NanoScope software.

Optical microscopy The capillary was placed under a stereo microscopy (Olympus SZX10-ACH1X) using a transmitted light source (Olympus SZX2-ILLT (LED)) at the bottom. This light source provided an even and diffuse illumination on the capillary from the bottom and created a neutral background for the image shooting. An external cold light source (Schott

KL1600LED) was placed in line with the capillary tube to enhance the internal reflections. The images were taken with a Nikon camera (DS-Fi2 with a DS-L3 controller).

Figure 2.1: Schematic drawing of the fabrication procedure. (1) Coating a PR layer on the inner capillary wall. (2) UV exposure under a patterned mask. (3) Removing the exposed PR layer using developer. (4) Hydrophobizing the inner surface with organosilane coating. (5) Removing PR layer with solvents.

2.3 Results

2.3.1 Hydrophobization by silicon oil

Arayanarakool and coworkers have developed a simple and clean method to hydrophobize micro- and nanofluidic networks by UV-patterning of silicon oil. The method combines a surface pre-treatment by oxygen plasma with UV irradiation. The mechanism is claimed as that oxygen plasma firstly generates active hydroxy groups at the glass surface and increases the surface energy. Silicon oil is physically adsorbed on the glass surface due to the van der Waals attraction and hydrogen bonds between oxygen atoms in the polymer backbone and the silanol groups on the glass surface [28]. The sequent UV irradiation is capable of breaking chemical bonds and generates radicals of oil molecules, which forms covalent bonds with the hydroxy groups on the glass surface. The terminal groups of silicon oil towards air provides a stable hydrophobic layer. Therefore, this process

2.3. Results

is reasonable for selective hydrophobization in enclosed microchannels by tuning the locations of the microchannels for UV irradiation.

We have attempted to apply positional-hydrophobization into microchannels using silicon oil and selective UV exposure on glass and silicon slides using a photomask. However, homogeneously hydrophobized surfaces of both substrates were obtained by means of contact angle measurements. Diffusion of oil from UV exposed surfaces to the covered area could be ruled out, based on diffusive transport rates. A simple experiment was then performed. Four groups of cleaned glass slides were put into petri dishes filled with silicon oil. Group 1 and 3 were exposed to UV irradiation in an UV box directly and Group 2 and 4 were firstly wrapped with alumina foil and then placed in the same UV box. Here the slides of group 1 and 2 were performed with oxygen plasma pre-treatment and group 3 and 4 were not. The measured contact angles on the modified surfaces are displayed in Table 2.1. As can be seen, our results agree with that of the reference paper that using oxygen plasma effectively enhances the reaction and results in an increased contact angle ($> 80^\circ$). But differently, the covered glass shows a contact angle similar to the exposed ones, for both groups with and without plasma pre-treatment. It seems UV illumination is not the dominant factor to induce the reaction between the oil and the hydroxy groups on the glass surfaces. Such findings aroused our interests to further explore the mechanism of hydrophobization by silicon oil.

Table 2.1: Contact angle measurements on glass slides exposed and covered in an UV box for 2 h.

Contact angle ($^\circ$)	UV (+)	UV (-)
Oxygen Plasma (+)	85.05 ± 1.91	82.42 ± 3.51
Oxygen Plasma (-)	60.87 ± 6.16	53.72 ± 12.87

An increased temperature to 45°C of the silicon oil after the reaction was measured by Arayanarakool and similar thermal phenomena were observed during our experiments as well. For this reason, we assume temperature may play an important role in the reaction. A series of experiments were performed to evaluate the contributions of oxygen plasma, UV irradiation and temperature on the reaction as evaluated by means of contact angle measurements.

Figure 2.2 shows the resulting contact angles of the modified sur-

faces by different processes, without (a) and with (b) oxygen plasma pre-treatment. As displayed in Fig. 2.2(a), both UV and temperature treatments enhance the contact angles. The on-line temperature measurement indicates a fast temperature increase occurred at the first 40 min during UV treatment and the plateau was reached at 50 °C for longer reaction times. As such, the contact angle generated by UV irradiation is coupled with a thermal induced reaction at 50 °C. Apparently, such a combination results in lower contact angles on the modified surface than that obtained by thermal processes for temperatures higher than 60 °C. This implies temperature plays an important role in the reaction. The highest contact angle is reached at 80 °C. Tinny air bubbles were observed in the oil after the reaction in both of our and Arayanarakool's experiments. These bubbles may result from the reaction products and pre-absorbed water.

Figure 2.2: Comparison of static contact angle measurements on glass surfaces via different modification processes. (a) Processes without oxygen plasma pre-treatment. (b) Processes with oxygen plasma pre-treatment.

Similar trends of contact angles in time were observed for all the modification processes with oxygen plasma pre-treatment. As shown in Fig. 2.2(b), UV irradiation and 60 °C treatment result in higher contact angles when a plasma pre-treatment is combined. 80 °C treatment generates similar contact angles after 2 h reaction time but displays a faster reaction rate compared to the process without plasma pre-treatment. Patterning silicon oil to glass surfaces by using UV irradiation is not suitable for selectively hydrophobizing a glass surface due to the heat release by the UV lamp and long reaction time.

Figure 2.3 shows the resulting dynamic contact angles on the surfaces modified at 80 °C with and without plasma treatment, respectively. When reaction time is less than one hour, the modified surfaces without

plasma treatment gives relative lower advancing and receding contact angles than that on the surfaces modified with plasma treatment. When the reaction time is longer than 1 hour, equivalent dynamic contact angles and hysteresis were obtained for all the measurements. It is clear that 80 °C treatment shows the highest reaction rate and results in the highest contact angles among all the processes, even without involving an oxygen plasma treatment.

Figure 2.3: Static contact angle measurement at 80 °C, with plasma pre-treatment (–) and without (–). ACA stands for advancing contact angle and RCA stands for receding contact angle.

Noticeably, our obtained contact angles are lower than those of the reference results by using the same oil (AR 20 cSt, Sigma-Aldrich). The difference may be caused by the inhomogeneity of silicon oil from the manufactures. In our initial tests, similar contact angles by thermal treatments compared to that by UV irradiation from the reference paper have been obtained.

2.3.2 Positional patterning inside microchannels

We propose an alternative approach for spatial patterning inside a microcapillary tube. Alternating hydrophilic/hydrophobic segments were obtained by combining photolithography with SAM chemistry. The photolithography process defines the boundary of hydrophilic/hydrophobic regions by patterning a dense positive photoresist (PR) layer on the targeted hydrophilic regions. The formed PR layer is dense and resistant enough to protect the covered surfaces from the subsequent SAM formation step.

As outlined in Fig.2.1, a dense positive PR layer was coated on the inner wall of a hydrophilic micro-capillary. We defined the boundary between the hydrophilic/hydrophobic segments by exposing the PR-coated micro-capillary to parallel UV light under a photo-mask with a desired pattern. The UV-exposed PR layer was washed away using a developer solution to expose the targeted surfaces and dried. The wettability of the exposed surfaces was modified by flowing an organosilane solution. Finally, we expose the hydrophilic regions by flowing dehydrated hexane to remove the silane residues followed by a mixture of acetone and ethanol (1:1 v/v) to remove the PR layer.

We verified the feasibility of this approach using flat glass slides. The static water contact angles were measured to be $28 \pm 3^\circ$ and $108 \pm 3^\circ$ on hydrophilic and hydrophobic surfaces, respectively (see Fig.2.4). This demonstrates that the patterned PR layer is sufficient to act as a protective layer but also keeps these surfaces relatively hydrophilic after removed. This allows to apply a second surface modification afterwards. It is important to note that a careful cleaning procedure is essential to remove all the unreacted silanes before removing the PR layers to ensure that the targeted hydrophilic surfaces stay intact. Atomic Force Microscopy (AFM) measurements demonstrate that there were no large aggregates and defects on the modified surfaces. The boundary between the modified and unmodified surfaces is very sharp. The formed SAM layer is highly uniform with a measured thickness ≈ 1 nm. The resulting difference in channel radius can be ignored. We have applied various silane chemistries for the hydrophobization process via both liquid (L) and gas (G) phase reactions. Different surface wettabilities were obtained as $75 \pm 2^\circ$ by Chlorotrimethylsilane (CTMS, G) and $100 \pm 4^\circ$ by triethoxyoctylsilane (OTES, L), respectively, with similar contact angles for all the hydrophilic regions.

Conducting a photolithography process inside a capillary tube is more challenging than on a flat surface. Coated PR layers with strong adhesion onto the channel wall and uniform thickness are essential. Strong adhesion of the PR layers effectively protects the desired pattern from the shear force caused by the rinsing solutions. It is reported that a cleaned substrate without surface water is of the primary importance to strengthen the adhesion of the PR layers. The presence of surface water may lift off the PR layer during developing and devastate the desired pattern [29, 30]. Primers or adhesion promoters are applied onto cleaned glass or silicon substrates as barrier to separate PR layers from the surface water [31].

Figure 2.4: Height profiles of a modified flat glass sample measured by AFM and their corresponding contact angles.

Figure 2.5: (a) Patterned capillaries after developing process, 600 μm . (b) Patterned capillary tube after developing process, 60 μm . (c) Water adhesion in a capillary tube after modification. HP-hydrophilic, HB-hydrophobic

Silazanes and silanes, such as hexamethyldisilazane (HMDS), are used as standard primers in cleanroom processes. However, it is inadequate to use these primers in our work. The primer forms a covalent bond to glass or silicon substrates and hydrophobizes the complete channel surfaces. This hinders the subsequent SAM formation and hydrophobizes the targeted hydrophilic segments. Moreover, PR droplets can form on such surfaces in a capillary after baking due to the low surface energy of the primer layers. The thickness difference caused by the droplets devastates the pattern structures since the developing rate is a function of the depth into the PR layers [32]. In this case, an adequate baking step, vacuum baking, is essential to be employed to remove the surface water. In order to ob-

tain a thin uniform PR coating, using diluted base solution for cleaning is desirable since it removes organic contaminations from glass. We have pre-rinsed the surface by using a TMAH solution to achieve this. Using TMAH avoids introducing extra contaminations since it is free of alkali metals. The optical images in Figure 2.5 (a) and (b) display the patterned capillary tubes after developing. The smallest pattern we have fabricated was $60\text{ }\mu\text{m}$ (Fig. 2.5(b)). As the fabrication is applied in a capillary tube, verifying the resulting surface wettability is challenging via contact angle measurement. We have attempted a facile method to test the modified tube by first filling it with DI-water and then gently blowing the water out with a nitrogen gas flow. Water resides on the hydrophilic segments over the hydrophobic segments (Fig. 2.5(c)).

2.4 Conclusion

To conclude, temperature is an important factor in the reaction between silicon oil and hydroxy groups on glass surfaces. A faster reaction rate and higher contact angle are obtained when the operating temperature is $\geq 60\text{ }^{\circ}\text{C}$, compared to that by UV irradiation. $80\text{ }^{\circ}\text{C}$ treatment shows the highest reaction rate and resulting contact angles among all the processes. Such findings provide a simplified hydrophobization process in micro- and nanochannels compared to the UV and plasma combined processes. Moreover, thermal induced hydrophobization makes silicon oil an potential material for a homogeneous hydrophobization of porous materials. Additionally, due to the long reaction time and non-local heating, this process is not suitable to pattern a glass surface with dissimilar wettability.

We have demonstrated positional patterning of surface wettability in a micro-capillary tube. The method is highly reproducible and efficient as multi-capillaries can be treated simultaneously. The modified micro-capillaries display a heterogeneous surface with very sharp boundaries between the hydrophilic and hydrophobic segments and excellent surface-uniformity. Our method can be employed to modify enclosed channel surfaces by various surface chemistries. The robust and inert characteristics of the SAM layer allows a secondary modification step on the initially protected hydrophilic surfaces. The smallest achieved dimension is $60\text{ }\mu\text{m}$. This limitation is likely to be reduced by introducing a liquid with a similar refractive index as that of the capillary material to reduce the light

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scatting during exposure.

Bibliography

- [1] Lam KF, Sorensen E, Gavriilidis A (2013) Review on gas–liquid separations in microchannel devices. *Chem Eng Res Des* 91:1941–1953.
- [2] Atencia J, Beebe DJ (2005) Controlled microfluidic interfaces. *Nature* 437:648–655.
- [3] Shui L, van den Berg A, Eijkel JC (2009) Interfacial tension controlled w/o and o/w 2-phase flows in microchannel. *Lab Chip* 9:795–801.
- [4] Shui L, Eijkel JC, van den Berg A (2007) Multiphase flow in microfluidic systems—control and applications of droplets and interfaces. *Adv Colloid Interface Sci* 133:35–49.
- [5] Ulman A (1996) Formation and structure of self-assembled monolayers. *Chem Rev* 96:1533–1554.
- [6] Gooding JJ, Mearns F, Yang W, Liu J (2003) Self-assembled monolayers into the 21st century: recent advances and applications. *Electroanalysis* 15:81–96.
- [7] Schreiber F (2000) Structure and growth of self-assembling monolayers. *Prog Surf Sci* 65:151–257.
- [8] Feng Y, Zhou Z, Ye X, Xiong J (2003) Passive valves based on hydrophobic microfluidics. *Sens Actuators A Phys* 108:138–143.
- [9] Oh KW, Ahn CH (2006) A review of microvalves. *J Micromech Microeng* 16:R13.
- [10] Maruyama T, et al. (2004) Liquid membrane operations in a microfluidic device for selective separation of metal ions. *Anal Chem* 76:4495–4500.

- [11] Tetala KK, Swarts JW, Chen B, Janssen AE, van Beek TA (2009) A three-phase microfluidic chip for rapid sample clean-up of alkaloids from plant extracts. *Lab Chip* 9:2085–2092.
- [12] Asanomi Y, Yamaguchi H, Miyazaki M, Maeda H (2011) Enzyme-immobilized microfluidic process reactors. *Molecules* 16:6041–6059.
- [13] Goto M, Tsukahara T, Sato K, Kitamori T (2008) Micro-and nanometer-scale patterned surface in a microchannel for cell culture in microfluidic devices. *Anal Bioanal Chem* 390:817–823.
- [14] Renberg B, et al. (2009) Serial dna immobilization in micro-and extended nanospace channels. *Lab Chip* 9:1517–1523.
- [15] Böhringer KF (2003) Surface modification and modulation in microstructures: controlling protein adsorption, monolayer desorption and micro-self-assembly. *J Micromech Microeng* 13:S1.
- [16] Lopez GP, Biebuyck HA, Harter R, Kumar A, Whitesides GM (1993) Fabrication and imaging of two-dimensional patterns of proteins adsorbed on self-assembled monolayers by scanning electron microscopy. *J Am Chem Soc* 115:10774–10781.
- [17] Feng X, Jiang L (2006) Design and creation of superwetting/antiwetting surfaces. *Adv Mater* 18:3063–3078.
- [18] Kim HC, et al. (2004) Photopatterned nanoporous media. *Nano Lett* 4:1169–1174.
- [19] Breisch S, de Heij B, Löhr M, Stelzle M (2004) Selective chemical surface modification of fluidic microsystems and characterization studies. *J Micromech Microeng* 14:497.
- [20] Priest C (2010) Surface patterning of bonded microfluidic channels. *Biomicrofluidics* 4:032206.
- [21] Chen C, Xu P, Li X (2014) Regioselective patterning of multiple sams and applications in surface-guided smart microfluidics. *ACS Appl, Mater Inter* 6:21961–21969.
- [22] Yamamoto M, et al. (2008) Patterning reactive microdomains inside polydimethylsiloxane microchannels by trapping and melting functional polymer particles. *J Am Chem Soc* 130:14044–14045.

- [23] Kaji H, Hashimoto M, Nishizawa M (2006) On-demand patterning of protein matrixes inside a microfluidic device. *Anal Chem* 78:5469–5473.
- [24] Vong T, et al. (2009) Site-specific immobilization of dna in glass microchannels via photolithography? *Langmuir* 25:13952–13958.
- [25] Derzsi L, Jankowski P, Lisowski W, Garstecki P (2011) Hydrophilic polycarbonate for generation of oil in water emulsions in microfluidic devices. *Lab Chip* 11:1151–1156.
- [26] Zhao B, Moore JS, Beebe DJ (2001) Surface-directed liquid flow inside microchannels. *Science* 291:1023–1026.
- [27] Arayanarakool R, Shui L, van den Berg A, Eijkel JC (2011) A new method of uv-patternable hydrophobization of micro-and nanofluidic networks. *Lab Chip* 11:4260–4266.
- [28] Marinova KG, Christova D, Tcholakova S, Efremov E, Denkov ND (2005) Hydrophobization of glass surface by adsorption of poly (dimethylsiloxane). *Langmuir* 21:11729–11737.
- [29] Levinson HJ (2005) Principles of lithography (SPIE Bellingham).
- [30] Glendinning WB, Helbert JN (2012) *Handbook of VLSI microlithography: principles, technology and applications* (William Andrew).
- [31] Brewer T, Flaim TD, Moss MG (1988). Adhesion promoting product and process for treating an integrated circuit substrate. US Patent 4,732,858.
- [32] Dill FH, Hornberger WP, Hauge PS, Shaw JM (1975) Characterization of positive photoresist. *IEEE Trans Electron Devices* 22:445–452.

Altering Emulsion Dynamics with Heterogeneous Surface Wettability

AN emulsion is a multiphase system in which one phase is suspended in the other immiscible phase in the form of small droplets. Due to its wide application in drug delivery, food processing, oil recovery, cosmetics and hazardous material handling, manipulating emulsion in terms of types, morphology and stability, is of vital importance. In this work, we demonstrate the influence of heterogeneous surface wettability on altering the emulsion dynamics using a single co-flow microfluidic devices. The oil-in-water emulsions were generated in a cylindrical glass capillary with a desired hydrophobic segment in the middle. Four scenarios of flow patterns, as intact, adhesion, inversion and break-up, were observed when oil droplets passed from a hydrophilic surface to an adjacent hydrophobic one. By analyzing our experimental results, we found a critical convective time scale, which delineates our parameter region for the unchanged and changing emulsion dynamics. Moreover, we characterized a critical capillary number Ca^* to depict the dynamic transition as a function of velocity and emulsion size using heterogeneous wetting surface, both experimentally and theoretically. Our results give insights on the controlling dynamics of emulsions in microfluidics by means of flow velocity and heterogeneous wettabilities, benefiting the application in biomedical and food processing.

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3.1 Introduction

An emulsion is a multiphase system in which one phase is suspended in the other immiscible phase in the form of small droplets. Due to its wide application in drug delivery [1–3], food processing [4, 5], oil recovery [6–8], cosmetics [9] and hazardous material handling [10], manipulating emulsion in terms of types, morphology and stability, is of vital importance. Conventionally, emulsions are prepared in large quantities using mechanical shear or agitation. The formed emulsions are highly polydisperse in size. Suitable emulsifiers, such as surfactants, are required to maintain their stabilities.

In contrast, the microsystem provides unprecedented control of individual droplet volumes dynamics and thus allows us to understand the underlying physics of emulsions [11, 12]. Mono-disperse or higher order emulsions can be produced using microfluidic devices as co-flowing [13, 14], T-,Y-junction [15], or flow focusing structure [16, 17] via shear flows between two immiscible phases [18–20]. When downscaling the channel dimension to microscale, which is close to the size of formed droplets, the gravity and inertial forces can be ignored due to small Weber and Bond numbers [21]. Instead, the viscous and interfacial forces become predominant as a result of the high surface-to-volume ratio. The capillary number Ca , representing the ratio of viscous to interfacial forces, is employed in characterizing the dynamics of emulsions formed in microsystem,

$$Ca = \mu U / \sigma \quad (3.1)$$

where μ (Pa·s) is the dynamic viscosity of the continuous phase, U (m s⁻¹) is the translational speed of the dispersing phase and σ (N m⁻¹) is the interfacial tension between the two phases. $Ca \sim U$ and varying Ca directly determines the size of formed emulsions, or even the mechanism as dripping or jetting in co-flow streams [18]. In the slug flow regime, the droplets flow surrounded by a thin lubrication film of the continuous phase. The film thickness h (on the order of magnitude of microns) is significantly determined by Ca [22–25]. Jose [23] investigated the dynamics of wetting droplets as a function of Ca by forming water-in-oil emulsions using a microfluidic flow-focusing structure. When Ca increases from 10^{-4} to 10, four different regimes can be classified: wetting ($h=0$), thin film ($h \rightarrow 0$), thick film ($h \sim Ca^{2/3}$ for $Ca > 10^{-1}$) and constant thicker film ($h/d=0.11$).

Besides, the liquid-solid interfacial tension is of high importance in altering the emulsion dynamics in microchannel. Modifying the inner surface wettability can enhance the wetting behavior of the continuous phase and prevents the adhesion of suspended inner phase, forming oil-in-water (o/w) or water-in-oil (w/o) emulsions [26, 27]. The majority of studies on microfluidic emulsions are conducted in microchannels of homogeneous wall wettability. Droplets show anomalous wetting behavior on a flat surface with dissimilar wettability [28–30]. Employing such surface into microchannels may lead to a significant influence on emulsion dynamics. Only a few studies has been conducted in this aspect due to the difficulties in patterning dissimilar wettability in an enclosed microchannel [26, 31]. Shui et al observed emulsion inversion using a microchannel patterned with adjacent hydrophobic and hydrophilic segments. Chen performed experiments in controlling adhesion of droplets by changing Ca using a capillary with similar design. He found a critical Ca for adhesion is correlated to the capillary dimension (d) and formed droplet size (D), $Ca \sim D^{3/4}/d^{3/2}$. However, due to the limitations in their surface modification, no information on emulsion transitions in between adhesion and inversion has been revealed. The influence of different surface energies on emulsion dynamics, which can be used to mimic the emulsion transport on a porous media, is still missing in the literature.

In this work, we demonstrate the influence of the heterogeneous surface wettability on altering the emulsion morphology and dynamics using a single co-flow microfluidic devices. The oil-in-water emulsions were generated in a cylindrical glass capillary with a desired hydrophobic segment in the middle, fabricated via the method described in Chapter 2. Using experiments and theoretical model, we address a critical convective time scale in controlling emulsion stability with heterogeneous wettability.

3.2 Experimental

3.2.1 Materials

Paraffin oil (Sinopharm Chemical), polyvinyl alcohol (PVA, MW=13000-23000 g mol⁻¹, Sigma-Aldrich) and Deionized (DI) water were used for the emulsion formation in a patterned micro-capillary tube.

3.2.2 Emulsion formation

Our co-flow microfluidic devices was built by carefully sliding a tapered micropipette into a circular glass capillary with inner diameter $d = 580 \mu\text{m}$ [14]. The oil-in-water emulsions were generated by injecting paraffin oil through the micropipette as inner phase and flowing aqueous solution (2 wt.% PVA) through the glass capillary as continuous phase. The droplets were formed in various morphologies in the capillary by controlling the flow rates of the inner oil phase (q_{in}) and outer aqueous phase (q_{out}) via two different syringe pumps. The corresponding dynamics of the microfluidic emulsion was visualized using a microscope (magnification $\approx 10\times$) equipped with a high-speed camera (Fig.3.1). The interfacial tension between the two liquid phases was measured as $\sigma = 15.2 \pm 0.7 \text{ mN/m}$ using the pendant drop method [32]. The dynamic viscosities of the oil and continuous aqueous phases were measured as $\mu_o = 21.5 \pm 0.1 \text{ mPa}\cdot\text{s}$ and $\mu = 2.0 \pm 0.1 \text{ mPa}\cdot\text{s}$, respectively, using a Rotational Rheometer (Physica MCR 301, Anton Paar).

The investigation on emulsion dynamics were first performed using a capillary with a homogeneous hydrophilic surface. The flow ratio, $\phi = q_{in}/q_{out}$, was fixed while varying q_{in} from 1 to $100 \mu\text{L}/\text{min}$. The resulting droplet length (D) and velocity (U) were measured from the captured images. Similar experiments were performed in a capillary with a 6 mm hydrophobic segment (λ) in the middle to investigate the influence of heterogeneous surface wettability. The fabrication method of such capillary is described in chapter 2 using n-Octyltriethoxysilane (OTES) via liquid induced hydrophobization process. The obtained static contact angles on flat glass surfaces were $27.3 \pm 3^\circ$ and $97 \pm 5^\circ$ on the hydrophilic and hydrophobic surfaces, respectively.

Figure 3.1: (a) Schematic diagram of a co-flow microcapillary device for the formation of oil-in-water emulsions. (b) The circular glass capillary contains a hydrophobic segment in 6 mm using OTES coating.

3.3 Results and Discussion

We first investigated the influence of flow rates on droplet morphologies using a capillary with a homogeneous hydrophilic surface. As can be seen from Fig. 3.2(a), the droplet length D increases with flow ratio ϕ but exhibits relative weak dependency on q_{in} . Small ϕ results in small droplets with nearly constant D for q_{in} ranging from 1 to 100 $\mu\text{L}/\text{min}$. Larger ϕ produces larger droplets with higher fluctuation in D , e.g. $\phi=7$. This is attributed to its larger surface area and thus energy of large oil droplets. As q_{in} indicates the absolute flow velocity, our results reveal that the droplet size exhibits a relative weak dependency on Ca for a fixed ϕ . This finding is in a agreement with previous works [33].

To validate the droplet size D as a function of ϕ , we performed a set of experiments by fixing q_{out} at 10 $\mu\text{L}/\text{min}$ while varying q_{in} ranging from 1 to 100 $\mu\text{L}/\text{min}$. Figure 3.2(b) shows the dependence of the normalized droplet size D/d on ϕ . When ϕ varies from 2 to 10, the dimensionless droplet size D/d varies with ϕ according to $D/d \sim \phi^{1.10}$ via a best power-law fit. Since q_{out} is kept as constant, ϕ is proportional to q_{in} . A correlation of $\phi \sim D$ can be obtained as q_{in} is also proportional to the droplet volume V_D , which can be estimated by $V_D = \pi d^2 D/4$. This correlation is consistent with our experimental data since d is constant in our case. The reason of the slightly higher power of 0.1 may be attributed to the thickness of the lubrication film. In contrast, when ϕ ranges from 0.1 to 1, the normalized droplet size D/d is nearly equal to the channel dimension d , $D/d \approx 1.1$, indicating an insignificant dependence on ϕ . Multiple reasons may result in this limited droplet size at small ϕ , such as large tip diameter [15, 34] or the viscosity of the two phases preventing the formation of droplets smaller than 600 μm .

To investigate the influence of surface wettability on emulsion dynamics, we formed droplets through a capillary with a 6 mm hydrophobic segment ($\lambda = 6\text{mm}$) in the middle. Since the droplet size is primarily determinant by ϕ , we gradually decreased the absolute flow rates of q_{in} and q_{out} while keeping ϕ constant. The resulting velocities of formed oil droplets (U) ranges from 3.6×10^{-6} to $7.0 \times 10^{-2} \text{ m s}^{-1}$ and the corresponding Ca ranges from 4.95×10^{-5} to 0.1.

Figure 3.3 shows the phase diagram of emulsion dynamics, when passing from a hydrophilic to a hydrophobic surface (highlighted in red).

3.3. Results and Discussion

Figure 3.2: (a) Droplet length (D) as a function of the oil flow rate (q_{in}) for different flow ratios (ϕ) in an unmodified, hydrophilic capillary. (b) Effect of flow ratio on normalized droplet length D/d . The dash line is the best fit of the power-law relation: $D/d \approx \phi^s$, $s = 1.1$.

The heterogeneous wetting wall has a strong influence on the emulsion morphology and motion. Stable oil droplets were first formed in the hydrophilic side surrounded by a thin aqueous lubrication film. After entering the hydrophobic region, the droplet behavior is altered depending on the flow rate and droplet size and exhibited in the following scenarios: (i) passing oil-in-water droplets without changing their size nor speed, (ii) adhesion of oil-droplets on the hydrophobic wall with an increasing advancing contact angle, (iii) inversion to a water-in-oil emulsions, and (iv) break up of the oil droplets with unstable lubrication films.

The emulsion dynamics among these four scenarios are summed in Fig. 3.3(b) in terms of Ca and D/λ . This figure indicates the existence of a critical capillary number Ca^* , or droplet speed ($Ca \sim U$), which delineates the parameter regions of changing and unchanged droplet dynamics for all operated ϕ between 0.1 and 11, as indicated by the dash line in the figure. When the Ca and D lie above this dash line, in the yellow color region, the oil droplets remain intact after passing the hydrophobic segment. In contrast, when Ca and D correlate below this line, the formed oil droplets alter their morphology as the oil phase contacts the hydrophobic wall, resulting in adhesion, inversion and break-up. In detail, for relative small droplets generated with ϕ ranging from 0.1 to 1, the oil-in-water emulsion remain intact when passing the hydrophobic region at high speed, or high Ca , whereas adhere on the hydrophobic wall at low speed. As the droplet size has an insignificant dependency on the droplet speed according to Fig. 3.2(b) for this ϕ range, the critical capillary number Ca^* is nearly

Figure 3.3: (a) Phase diagram of o/w emulsion dynamics after passing a hydrophobized section (highlighted in red along the capillary). (b) Summed emulsion dynamics in terms of Ca and D/λ .

constant for these three data sets. While adhering, the oil droplets display a measured contact angle hysteresis as $73 \pm 10^\circ$, for ϕ ranging from 0.1 to 5 (Fig. 3.3(ii)). For relative larger droplets generated at ϕ ranging from 3 to 11, the critical capillary number Ca^* increases with D/λ . Above this Ca , the droplets still remain intact, whereas below this Ca , these droplets start to invert into w/o emulsions or break-up irreversibly. These phase transitions, inversion and break up, devastate the initial thin water-film on the hydrophilic wall and result in oil film residual along the hydrophobic wall.

The critical capillary number Ca^* , corresponding to the critical velocity of the oil droplets, can be expressed in terms of droplet size, as shown in Fig. 3.4(a). Based on our experimental conditions, the correlation is found to be $Ca^* = \alpha(D/\lambda)^\beta$, with the best fit of the scaling power $\beta = 1.40 \pm 0.12$ and prefactor $\alpha = 4.5 \times 10^{-4} \pm 7.0 \times 10^{-5}$.

It is important to realize that this critical boundary in Fig. 3.3 reveals a universal, critical time scale, Δt^* , for each ϕ . We addressed this Δt^* by defining a characteristic timescale $\Delta t = D/U$, the droplet convective timescale, which corresponds to the life-time of the thin wetting

Figure 3.4: (a) Critical capillary number for the oil droplets to cause adhesion on the hydrophobic surface in the capillary. The dash line indicates a power-law fit of $Ca^* \sim (D/\lambda)^\beta$, where λ is the length of the hydrophobized session, $\approx 10 d$. (b) Convective time scale Δt of the o/w emulsions for different flow ratios. The dash line indicates the average critical convective time Δt^* of the oil droplets.

film produced by the passage of the droplet in the initial hydrophilic region. By expressing Δt for different ϕ based on the results from Fig.3.3, the value of Δt^* can be estimated as depicted in Fig.3.4(b). For each ϕ , when $\Delta t > \Delta t^*$, the oil droplets change their dynamic and morphologies. When $\Delta t < \Delta t^*$, the droplet remains intact. We experimentally found that this Δt^* is universal for all the operated ϕ in our work: $\Delta t^* = 3.0 \pm 1.1$ s. This critical timescale Δt^* can be associated with the typical dewetting timescale of the local thin lubrication film due to the changes in wettability. The stability of the wetting film relies on its life time. For instance, unstable thin films are obtained for large and slow-moving droplets, having a thin film lifetime greater than its dewetting timescale: $\Delta t > \Delta t^*$, and thus ruptured.

Apparently, this dewetting time scale is associated with the heterogeneity of the surface wettability. A higher difference in the wettability between the hydrophilic and hydrophobic surfaces rises the affinity of oil droplets to the hydrophobic surfaces, thus results in a shorter dewetting time. In our experiments, we observed that altering emulsion dynamics occurred along with reducing the aqueous lubricating thin film in thickness to almost zero, i.e., when oil droplets adhere to the hydrophobic wall. The thickness of the thin film (h) in the hydrophilic region is $6 \mu m$. This thickness is larger than the interaction range of the van der Waals force, so no rupture occurred. Differently, the changing of emulsion dynamics results in a very thin lubrication film, $h \approx O(1 \mu m)$ range. This leads to an increase in the attractive force between the oil phase and hydrophobic

wall, causing thin film rupture.

We address the empirical power-law relation of the Ca^* using a simplified theoretical model. The rupture of the thin film can occur when the film is thin enough to enter the interaction range of the van der Waals force. As such, the suspended droplets are pulled to the solid wall when the van der Waals force is equal to or larger than the Laplace pressure. The Laplace pressure can be estimated by considering the oil-water interface as nearly cylindrical (of size D), but slightly perturbed with a modulation amplitude of the order of magnitude of the film thickness h , where

$$\Delta P = \frac{\sigma}{D^2/h} \quad (3.2)$$

The van der Waals force between the oil phase and the hydrophobic wall can be described by the disjoining pressure, as a function of the film thickness h and the Hamaker constant A [35],

$$\Pi(h) = \frac{A}{6\pi h^3} \quad (3.3)$$

When $\Pi(h) \gtrsim \Delta P$, the thin lubrication film ruptures and we can obtain a scaling relation of $D^2/\sigma \sim h^4$ at the transition point [31]. Here, we use an empirical relation of the thin film thickness $h/d \sim Ca^{0.354} We^{0.097}$, instead of using the classical Taylor ($h \sim Ca^{1/2}$) or Bretherton ($h \sim Ca^{2/3}$) thin-film equations [6, 36] since this scaling relation has a slight Weber-number (We) weighting modification of the Bretherton description and gives a better approximation of various data than previous models, for wide ranges of Reynolds and Weber numbers. The We and Re , regarding the parameters of the oil droplets in our work, range from 5×10^{-8} to 2×10^{-1} and from 10^{-4} to 2, respectively. Thus, the critical condition of $Ca^* \sim D^{1.41}$ is obtained. This correlation agrees with our experimental results, $\beta = 1.40$. However, a rigorous theory that quantifies the contribution of heterogeneous surface wettability, such as static or dynamic contact angles, is still missing in the literature.

3.4 Conclusion

We investigated the influence of heterogeneous surface wettability on altering the emulsion dynamics using a single co-flow microfluidic devices.

Four scenarios of flow patterns, as intact, adhesion, inversion and break-up, were observed when oil droplets passed from a hydrophilic surface to an adjacent hydrophobic one. By analyzing our experimental results, we found a critical convective time scale, Δt^* , which delineates our parameter region for the unchanged and changing emulsion dynamics. A fast moving droplet, which results in relative thick and stable lubrication film with a life time $\Delta t < \Delta t^*$, keeps intact in emulsion size and velocity when passing the heterogeneous wetting surface. In contrast, droplets traveling with slow speeds result in a thinner lubrication film with a life time $\Delta t > \Delta t^*$, altering the emulsion dynamics in terms of adhesion, inversion or break-up. Corresponding to the Δt^* , we characterized a critical capillary number Ca^* to depict the dynamic transition as a function of velocity and emulsion size both experimentally and theoretically. Our results give insights on the controlling dynamics of emulsions in microfluidics by means of flow velocity and heterogeneous wettabilities, benefiting the application in biomedical and food processing.

Bibliography

- [1] Dams SS, Walker IM (1987) Multiple emulsions as targetable delivery systems. *Methods Enzymol* 149:51–64.
- [2] Nakano M (2000) Places of emulsions in drug delivery. *Adv Drug Delivery Rev* 45:1–4.
- [3] Vasiljevic D, Parojcic J, Primorac M, Vuleta G (2006) An investigation into the characteristics and drug release properties of multiple w/o/w emulsion systems containing low concentration of lipophilic polymeric emulsifier. *Int J Pharm* 309:171–177.
- [4] Muschiolik G (2007) Multiple emulsions for food use. *Curr Opin Colloid Interface Sci* 12:213–220.
- [5] Leal-Calderon F, Thivilliers F, Schmitt V (2007) Structured emulsions. *Curr Opin Colloid Interface Sci* 12:206–212.
- [6] C TK, F HB (2009) *Emulsions in Enhanced Oil Recovery*, volume 231 (Advances in Chemistry).
- [7] Schramm LL (1992) Fundamental and applications in the petroleum industry. *Adv Chem* 231:3–24.
- [8] Huang JS, Varadaraj R (1996) Colloid and interface science in the oil industry. *Curr Opin Colloid Interface Sci* 1:535–539.
- [9] Yoshida K, Sekine T, Matsuzaki F, Yanaki T, Yamaguchi M (1999) Stability of vitamin a in oil-in-water-in-oil-type multiple emulsions. *J Am Oil Chem Soc* 76:1–6.

- [10] Ouyang Y, Mansell R, Rhue R (1995) Emulsion-mediated transport of nonaqueous-phase liquid in porous media: A review. *Crit Rev Env Sci Technol* 25:269–290.
- [11] Baroud CN, Gallaire F, Dangla R (2010) Dynamics of microfluidic droplets. *Lab Chip* 10:2032–2045.
- [12] Seemann R, Brinkmann M, Pfohl T, Herminghaus S (2012) Droplet based microfluidics. *Rep Prog Phys* 75:016601.
- [13] Cramer C, Fischer P, Windhab EJ (2004) Drop formation in a co-flowing ambient fluid. *Chem Eng Sci* 59:3045–3058.
- [14] Shah RK, et al. (2008) Designer emulsions using microfluidics. *Materials Today* 11:18–27.
- [15] Nisisako T, Torii T (2008) Microfluidic large-scale integration on a chip for mass production of monodisperse droplets and particles. *Lab Chip* 8:287–293.
- [16] Anna SL, Bontoux N, Stone HA (2003) Formation of dispersions using "flow focusing" in microchannels. *Appl Phys Lett* 82:364–366.
- [17] Ward T, Faivre M, Abkarian M, Stone Ha (2005) Microfluidic flow focusing: Drop size and scaling in pressure versus flow-rate-driven pumping. *Electrophoresis* 26:3716–3724.
- [18] Utada AS, Fernandez-Nieves A, Stone Ha, Weitz Da (2007) Dripping to jetting transitions in coflowing liquid streams. *Phys Rev Lett* 99:1–4.
- [19] Stone HA, Stroock AD, Ajdari A (2004) Engineering flows in small devices: microfluidics toward a lab-on-a-chip. *Annu Rev Fluid Mech* 36:381–411.
- [20] Garstecki P, Stone Ha, Whitesides GM (2005) Mechanism for flow-rate controlled breakup in confined geometries: A route to monodisperse emulsions. *Phys Rev Lett* 94:1–4.
- [21] Günther A, Jensen KF (2006) Multiphase microfluidics: from flow characteristics to chemical and materials synthesis. *Lab Chip* 6:1487–1503.

- [22] Hodges S, Jensen O, Rallison J (2004) The motion of a viscous drop through a cylindrical tube. *J Fluid Mech* 501:279–301.
- [23] Cubaud T (2009) Wetting and lubricating film instabilities in microchannels. *Phys Fluids* 091103:128–129.
- [24] Kuzmin a, Januszewski M, Eskin D, Mostowfi F, Derksen JJ (2011) Three-dimensional binary-liquid lattice boltzmann simulation of microchannels with rectangular cross sections. *Chem Eng J* 178:306–316.
- [25] Eain MMG, Egan V, Punch J (2013) Film thickness measurements in liquid-liquid slug flow regimes. *Int J Heat Fluid Flow* 44:515 – 523.
- [26] Shui L, van den Berg A, Eijkel JC (2009) Interfacial tension controlled w/o and o/w 2-phase flows in microchannel. *Lab Chip* 9:795–801.
- [27] Wan J, Bick A, Sullivan M, Stone HA (2008) Controllable microfluidic production of microbubbles in water-in-oil emulsions and the formation of porous microparticles. *Adv Mater* 20:3314–3318.
- [28] Naidich YV, Voitovich RP, Zabuga VV (1995) Wetting and spreading in heterogeneous solid surface-metal melt systems. *J Colloid Interface Sci* 174:104–111.
- [29] Drelich J, Wilbur JL, Miller JD, Whitesides GM (1996) Contact angles for liquid drops at a model heterogeneous surface consisting of alternating and parallel hydrophobic/hydrophilic strips. *Langmuir* 12:1913–1922.
- [30] Morita M, Koga T, Otsuka H, Takahara A (2005) Macroscopic-wetting anisotropy on the line-patterned surface of fluoroalkylsilane monolayers. *Langmuir* 21:911–918.
- [31] Chen H, Dong E, Li J, Stone HA (2013) Adhesion of moving droplets in microchannels. *Appl Phys Lett* 103:131605.
- [32] De Gennes PG, Brochard-Wyart F, Quéré D (2013) *Capillarity and wetting phenomena: drops, bubbles, pearls, waves* (Springer Science & Business Media).
- [33] Baroud CN, Tsikata S, Heil M (2006) The propagation of low-viscosity fingers into fluid-filled branching networks. *J Fluid Mech* 546:285–294.

- [34] Utada AS, Fernandez-Nieves A, Gordillo JM, Weitz Da (2008) Absolute instability of a liquid jet in a coflowing stream. *Phys Rev Lett* 100:1–4.
- [35] Butt HJ, Graf K, Kappl M (2006) *Physics and chemistry of interfaces* (John Wiley & Sons).
- [36] Bretherton F (1961) The motion of long bubbles in tubes. *J Fluid Mech* 10:166–188.

Performance Study of Pervaporation in a Microfluidic System for the Removal of Acetone from Water

VOLATILE organic compounds (VOCs) removal from water suffers from mass transport limitations due to depletion of the minor component at the membrane surface. Understanding of such mass transport limitations is crucial for the development of novel pervaporation membranes and methods. In this work, we present a performance study on the removal of trace amount of acetone from water via pervaporation to provide insight on mass transport limitations. We used glass microfluidics containing a thin polydimethylsiloxane (PDMS) membrane that allows very fast removal of acetone from water. High acetone removal efficiency of 81% is achieved for just 3 minutes residence time at room temperature for a 35 μm thin membrane. A design criterion based on intrinsic system parameters is derived to engineer the pervaporation system for both micro- and macro-scales. Our micro-PV device shows promising potential regarding the characterisation of pervaporation processes and materials for the removal of VOCs from water.

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4.1 Introduction

The broad ranges of functionality and versatility of microchemical systems has promoted their transformation from simple devices, like micro-reactors [1–3], micro-mixers [4, 5], and micro-separators [6, 7], to complex multi-step integrated networks [8–11]. Developing a continuous multi-step microchemical synthesis is of particular interests nowadays. Moreover, such systems provides fundamental insight regarding the mass transport kinetics.

Separating immiscible liquids in microdevices has been intensively investigated exploiting capillary phenomena which become stronger at smaller length scales [12, 13]. Separating miscible liquids requires different approaches. Trace removal of volatile organic compounds (VOCs) from water inherently suffers from mass transport limitations posing challenges regarding fast and complete purification. Few studies have attempted to accomplish microfluidic separation by implementing membrane technology [14, 15]. Zhang et al. [14] reported membrane distillation in a microfluidic system to separate water-methanol mixtures. By generating a temperature gradient in a stacked microdevice, methanol vapour was separated from water and collected in a cooling channel. Kaufman et al. [15] fabricated a high pressure microfluidic cell for Nanofiltration/Reverse Osmosis separation. They have investigated the performance of the device via both experiments and simulation and concluded that a shallower channel is beneficial for minimising concentration polarisation. In addition to these membrane technologies in microdevices, pervaporation (PV) seems another interesting but relatively unexplored candidate.

PV is an efficient membrane process to separate minor components from liquid mixtures by partial vaporisation and permeation. Such process is performed by bringing a liquid mixture in contact with one side of a membrane while a vacuum or a sweeping gas is applied to the other side. Species with higher affinities for the membrane, diffuse preferentially through the membrane and vaporise at the other side of the membrane. The created concentration gradient or the partial pressure difference across the membrane is the driving force for the separation process. The advantages of PV, regarding energy requirements and simple process control, allow for competitive applications like separating VOCs from water, aqueous acrylic latex, dehydrating organic solvents, and organic-organic solvent separation [16–19]. The study of VOC pervaporation using microfluidic devices is of

particular interest due to the notorious concentration polarisation, or depletion, resulting in severe mass transport limitations.

Implementing pervaporation into microfluidic devices has been accomplished in some examples [20–23]. Transport of water through a polydimethylsiloxane (PDMS) layer was used to investigate concentration profiles and phase diagrams of the retained solute [21, 24, 25]. Ziemecka has recently reported progress on concentrating hydrogen peroxide by pervaporation in a microfluidic device by varying the process temperatures. The experimental results closely resembled their 1D modelling work. No investigation on the mass transport resistance was reported in their study [23]. Among these studies, PDMS membranes are commonly selected as a results of their properties including optical transparency, ease of integration into microdevices and low-cost.

The mass transport mechanisms of PV systems can be described in various models according to the selection of dense or porous membranes [26–29]. The resistance-in-series model is widely accredited in describing the mass transport for dense membrane pervaporation systems under steady state. Three serial mass transfer resistances are defined in this model (Eq.(1) and (2)); the resistance in the feed liquid ($1/k_l$), that across the membrane ($1/k_m$) and that in the membrane permeate ($1/k_p$). The $1/k_p$ is normally neglected due to relatively fast transport in the gas phase. The permeation flux J_m of the migrating species in the system can be defined as

$$J_m = k_{ov}(c_l - c_p) = k_l(c_l - c_{l,m}) = k_m(c_{l,m} - c_{m,p}) \quad (4.1)$$

where c_l , c_p , $c_{l,m}$ and $c_{m,p}$ ($mole\ m^{-3}$) are the species concentrations in the feed bulk, in the permeate phase, at the feed-membrane interface and at the membrane-permeate interface, respectively. k_{ov} ($m\ s^{-1}$) is the overall mass transfer coefficient. The inverse of a mass transfer coefficient is the respective resistance:

$$\frac{1}{k_{ov}} = \frac{1}{k_l} + \frac{1}{k_m} = \frac{l}{D} + \frac{\delta}{D_m} \quad (4.2)$$

where δ is the membrane thickness, D_m is the species diffusion coefficient in the membrane, D is its diffusion coefficient in the solvent, and l is the thickness of the concentration boundary layer in the liquid feed.

The values of k_m and k_l allow comparisons of process performances, as well as evaluations of mass transfer efficiency for different configurations. It is important to notice that k_l varies with the dynamics of the feed solution and k_m depends on the intrinsic membrane characteristics. Côté and Lipski [30, 31] are among the first to propose that the mass transfer of a PV system is particularly limited by diffusion of the solute in the liquid-membrane boundary layer. The reason lies in the long diffusion length or low concentration gradient between the bulk to the membrane boundary which cause strong concentration polarisation. Depletion in the boundary layer can dominate the performance [32]. In particular, Wijmans shows that concentration polarisation already dominates at very low Peclet (Pe) numbers for the removal of trace compounds by PV [33]. In such a case, membrane selection is less critical. Relative thick rubber membranes are sufficient and preferable over thinner composite materials due to the advantages in low-cost and low water permeability. Li et al. [34] have investigated operation parameters on the PV performance using a composite PDMS membrane to separate a variety of organic solvents from water. Their results have shown a high dependence of the dominant resistance region on the solvent properties, particularly in its partition coefficient. In their investigated flow rate range, methanol transfer is limited by the k_m whereas acetone transfer is determined by both k_m and k_l .

In this study, we aim to conduct a performance study for the removal of acetone from water to provide the insights on the mass transport mechanisms. The used microfluidic format provides excellent mass transport in the boundary layer, which allows adequate membrane performance assessment. A thin layer of PDMS membrane was selected for its high selectivity for VOCs in a low concentration range [35, 36]. Via modelling and experiments, we quantitatively investigated the local mass transfer coefficients of acetone through the liquid boundary layer (k_l) and the membrane (k_m) by varying membrane thicknesses and feed flow rates. An optimisation based on the intrinsic system parameters is proposed to identify the rate limiting region and engineer the design for both micro- and macro-scale pervaporation.

4.2 Experimental

4.2.1 Microchips preparation

Glass slides

The microchannels for liquid flow (L-channel) and gas flow (G-channel) were fabricated on separate borofloat glass slides by standard photolithography followed by wet etching (Micronit B.V.). The depth (H) and length (L) of both channels were $50\text{ }\mu\text{m}$ and 0.26 m , respectively. The width of the L-channel was $350\text{ }\mu\text{m}$ and the G-channel was $600\text{ }\mu\text{m}$ to facilitate channel alignment during manual assembly (Fig. 4.1(a)). The glass slides were diced in the size of $1.5\text{ x }4.5\text{ cm x cm}$ for bonding.

PDMS membrane

The flat-sheet PDMS membranes were prepared by mixing the polymer and the crosslinking agent (TRV 615 A+B, Momentive, Columbus, Ohio) in 10:1 weight ratio [37]. The mixture was first degassed in a desiccator and then cast onto a polished aluminium plate at controlled thickness. The films were cured at 80° for 2 h in a nitrogen-flushed oven and then placed in a nitrogen box overnight. The resulting membrane thicknesses were measured by a Micrometer (Coolant Proof) at multiple spots of the membranes before bonding and varied between $35 - 270 \pm 5\text{ }\mu\text{m}$.

Membrane integration

A combined oxygen plasma and thermal-bonding method was employed to create leakage-free bonding between PDMS membrane and glass slides [38]. Two glass slides and a PDMS membrane were firstly cleaned and activated by oxygen plasma at 60 W, 40 s (Femto, Diener Electronic). The PDMS membrane was immediately contacted with one glass slide first and then to the other with manual alignment. The pre-bonded chip was clamped and placed in an oven to enhance the bonding strength at 80° for 2 h. The bonded chip was enclosed in a Micronit chip holder and connected (Upchurch connections) to the gas and liquid flow control. Both mass and concentration measurements at the in- and outlets were performed before each measurement to ensure a leakage-free operation of the microchip.

4.2.2 Experimental setup

The aqueous feed solutions were prepared by dissolving acetone (Sigma-Aldrich) in deionized water at 0.2 wt% and 0.4 wt% and pumped into the L-channel under flow rates (q_v) ranging from 1 to 10 $\mu\text{L min}^{-1}$ using a syringe pump (HARVARD Apparatus PHD 2000). The corresponding residence times (V/q_v , V is the channel volume) and Reynolds numbers (Re) range from 26 to 264 s and 0.08 to 0.84, respectively. A co-sweeping nitrogen flow was pumped through the G-channel under a constant feed pressure of 0.120 bar (Bronkhost EL-PRESS). This pressure has been verified experimentally to ensure a gas flow independent acetone removal. The acetone concentration in the liquid outflow was detected by light absorbance measurement using an online UV-Vis spectrophotometer (Ocean optics, DH-2000). Acetone was selected as the target solute due to its unique absorption peak within the wavelength of UV-Vis range. The calibration curve was measured for concentrations from 0.01 to 0.8 wt% at the wavelength of 262.64 nm. Only feed concentrations lower than 0.4 wt % were prepared for the measurements as a result of their linear correlation to the corresponding absorbance in this range (Fig. 4.1(b)). All experiments were conducted at room temperature and for multiple runs. The sensitivity of the setup provided standard deviations that were smaller than the symbols used in the plots. The normalized average outlet concentration c_{out}/c_0 was determined to evaluate the acetone removal efficiency at various residence times and membrane thicknesses.

4.3 Modelling

A boundary flux condition describing the membrane transport, coupled with the convection-diffusion equation for the L-channel were used to investigate the mass transport evolution of acetone from the L-channel through the membrane. Fig. 4.2 illustrates the L-channel and the PDMS membrane with indicated transport resistances. The G-channel resistance was ignored by assuming a zero acetone concentration in the gas phase. It was reported that varying feed concentration and temperature has minor influence on the PDMS membrane selectivity between acetone and water [36]. Here, we consider only acetone migration through the PDMS membrane. The acetone flux through the membrane under steady state is proportional to the permeability P , the membrane thickness δ , and the partial vapour

pressure at the membrane surface p_l (Eq.(3)). The right-hand side of the Eq.(3) gives the solute flux arriving at the membrane wall from the bulk due to diffusion. The left hand side of the equation accounts for solute flux through the PDMS membrane.

Figure 4.1: (a) Schematic illustration of the glass chip with a thin layer of PDMS membrane in between. The concentration in the outlet is analysed online using UV-Vis spectroscopy. (b) Calibration curve for acetone relating the bulk concentration to its absorbance measured by UV-Vis.

$$J_m = \frac{P}{\delta} p_l = -D \frac{\partial c_l}{\partial y} \Big|_{y=H} \quad (4.3)$$

where D is the diffusion coefficient of acetone in water, and c_l the acetone concentration at the membrane. By using Henry's law, $K p_l = c_l$, where K is the Henry constant, we obtain a simple boundary condition for the convection diffusion domain (at $y = H$):

$$\frac{\partial c_l}{\partial y} \Big|_{y=H} = -\frac{P}{\delta K D} c_l \quad (4.4)$$

The factor $P/\delta K$ can be collapsed into the membrane mass transfer coefficient k_m . By implementing the channel configuration, the non-dimensional boundary condition for $y = H$ is obtained:

$$\frac{\partial \tilde{c}_l}{\partial \tilde{y}} \Big|_{\tilde{y}=1} = -\frac{H k_m}{D} \tilde{c}_l \quad (4.5)$$

4.3. Modelling

where $\tilde{y} = y/H$ and $\tilde{c}_l = c_l/c_0$. The dimensionless parameter Hk_m/D , which is the ratio of the membrane flux to the diffusive flux and defined as our performance number, fully determines the performance of the separation and can be used to understand and optimise the process. Realise that our performance number is equivalent to the second Damköhler number typically used for surface reactions, where we use k_m as the mass transfer rate of the membrane instead of a first order surface reaction rate constant.

Figure 4.2: Illustration of the 2D numerical model, assuming a parabolic velocity profile in the liquid phase, with purely advective transport in the x direction and only diffusion in the y direction.

As the acetone concentration is lower than 1 wt%, its presence in the bulk stream will not affect the density and the velocity profile of the flow significantly [39]. The transport in the liquid phase is governed by the convection diffusion equation ignoring axial diffusion:

$$u(y) \frac{\partial c_l}{\partial x} = D \frac{\partial^2 c_l}{\partial y^2} \quad (4.6)$$

where $u(y) = u_{avg}(-6y^2/H^2 + 6y/H)$ is the parabolic velocity profile. The convection diffusion equation is non-dimensionalised by introducing $\tilde{x} = x/L$, and previously introduced $\tilde{y}$ and $\tilde{c}_l$, to result in:

$$\frac{6u_{avg}H^2}{LD}(-\tilde{y}^2 + \tilde{y}) \frac{\partial \tilde{c}_l}{\partial \tilde{x}} = \frac{\partial^2 \tilde{c}_l}{\partial \tilde{y}^2} \quad (4.7)$$

Realize that the dimensionless factor on the left side of the Eq. (7), $u_{avg}H^2/LD$, equals the transverse Peclet number Pe_m times the ratio of height-to-length ($\alpha = H/L$) (Eq.(8)) [40]. This number represents the

ratio of timescales for diffusion in the normal ($\perp$) and advection in the tangential ($\parallel$ convection) direction.

$$\alpha Pe_m = \frac{t_{\perp}}{t_{\parallel}} = \frac{u_{avg} H^2}{LD} \quad (4.8)$$

Together with the dimensionless parameter from the boundary condition, Hk_m/D , these numbers indicate the different regimes for transport and possible concentration polarization significance. Steady state concentration profiles are computed by solving equations (7) with boundary condition (5) in Matlab for k_m values ranging from 10^{-6} to 10^{-8} m s $^{-1}$. The lower boundary, at $y = 0$ is considered as impermeable. The numerical results were fitted to the experimental results to extract the values of $k_{m,2D}$ for different membrane thicknesses.

4.4 Results and discussion

Due to the microfluidic dimensions and consequently well-defined flow conditions, the mass transport evolution of the PV system can be accurately studied. We have conducted a systematic study on the performance of the PV system by varying the feed concentration, membrane thickness and flow rate. Their influence on the separation efficiency has been investigated and represented in terms of k_m and k_l values. The comparison of k_m and k_l values indicates the dominant mass transport resistance, which allows an optimisation of the PV system.

We have first investigated the effect of feed concentration on the acetone separation efficiency. Fig. 4.3 reveals the evolution of c_{out}/c_0 as a function of residence time for membrane thicknesses of 35 and 270 μm , respectively. As can be seen, the inlet feed concentration has minor effect on the c_{out}/c_0 under the experimental conditions used [41]. This confirms a constant membrane permeability k_m for the different feed concentrations.

To determine the k_m values, we have prepared PDMS membranes with different thicknesses from the same batch to ensure a constant permeability. Fig. 4.4 reveals the influence of membrane thickness on the normalised outlet concentration c_{out}/c_0 as a function of residence time. The symbols represent the experimental results and lines are the fitted simulation results. Both the membrane thickness and residence times have

pronounced influence on the acetone separation efficiency.

The k_m values of each membrane thickness are extracted by fitting the 2D simulation results for residence times ranging from 53 to 170 s where the experimental results are most reliable. The weighted standard deviation is minimised as the optimisation function (Eq.(9)). The obtained k_m values range from 1.15 to $4.94 \cdot 10^{-7} \text{ m s}^{-1}$ for the indicated film thicknesses. These values are consistent with those of scaled PV systems. The extracted permeability of the PDMS membrane towards acetone is then on the order of $10^{-11} \text{ m}^2 \text{ s}^{-1}$ (comparable to $9 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for $8 \text{ } \mu\text{m}$ composite PDMS membrane [34].)

$$\sigma_w = \sqrt{\frac{\sum_{i=1}^n ((c_{exp} - c_{sim})/c_{exp})^2}{N - 1}} \quad (4.9)$$

Figure 4.3: c_{out}/c_0 against residence time for different feed concentrations and membrane thicknesses. Lines correspond to simulation results.

Since our 2D model includes the axial convection and transverse diffusion, we fully capture any depletion zone forming. A simpler 1D model can be applied when neglecting any normal concentration gradients (in the y direction), and the concentration is only a function along the x position in the channel. Such a 1D model describes convective transport in x -direction equals to the removal rate through the membrane:

Figure 4.4: c_{out}/c_0 against residence time with different membrane thicknesses. Symbols represent the experimental results and lines correspond to the fitted simulation results. $c_0 = 0.4$ wt%.

$$\frac{\partial c_l}{\partial t} = u_{avg} \frac{\partial c_l}{\partial x} = -k_{ov,1D} c_l \quad (4.10)$$

$$k_{ov,1D} \sim k_{m,1D} \frac{A_m}{V} \quad (4.11)$$

By integrating and considering the initial conditions $t = 0$ and $c = c_0$, the relation between c_{out} and residence time provides $k_{ov,1D}$ (s^{-1}). Realise that $k_{ov,1D}$ approaches $k_{m,1D} \frac{A_m}{V}$ if concentration polarisation becomes negligible (A_m is the membrane interfacial area). This occurs when the transverse diffusion is much faster than the membrane permeation. The $k_{m,1D}$ ($m s^{-1}$) values can therefore be extracted from the experimental data by simple curve fitting using Eq.(10):

$$k_{m,1D} = -\frac{V}{A_m} \cdot \frac{1}{t} \cdot \ln \frac{c_{out}}{c_0} \quad (4.12)$$

Table 4.1 displays the values of $k_{m,1D}$ and $k_{m,2D}$ for different membrane thicknesses. For the thicker membranes, $k_{m,1D}$ converges to $k_{m,2D}$, which indicates that concentration polarisation becomes negligible.

Realise that our $k_{m,1D}$ consists of the resistances of both the membrane and the boundary layer. k_l can therefore be estimated from Eq.(2)

4.4. Results and discussion

Table 4.1: Comparison of the k_m values in between 1D and 2D models.

Membranes (μm)	k_m 2D (m s^{-1})	k_m 1D (m s^{-1})
35	$4.94 \cdot 10^{-7}$	$4.69 \cdot 10^{-7}$
50	$2.44 \cdot 10^{-7}$	$2.40 \cdot 10^{-7}$
85	$1.57 \cdot 10^{-7}$	$1.55 \cdot 10^{-7}$
145	$1.15 \cdot 10^{-7}$	$1.15 \cdot 10^{-7}$

giving values ranging from 10^{-6} to 10^{-5} m s^{-1} . This confirms little concentration polarisation in our system and suggests that our microfluidic PV would benefit from thinner, composite, pervaporation membranes, as opposed to large scale pervaporation processes. For thick membranes, one can determine k_m directly from the 1D equation, where for thin membranes one needs to include the 2D equations that include information on the depletion zone.

A comparison of k_m with k_l reveals that, the acetone separation becomes diffusion limited for very thin (e.g. composite) PDMS membranes. In such cases, k_m approaches k_l around 10^{-6} m s^{-1} and generates a highly efficient pervaporation system. These results demonstrate the advantages of using a microfluidic device in terms of its efficient mass transport caused by relatively short diffusion distances. Further reducing the channel height will benefit the separation process only when k_l is comparable or smaller than k_m .

Figure 4.5 displays the concentration profile within the liquid phase as numerically obtained for $k_m = 4.94 \cdot 10^{-7} \text{ m s}^{-1}$, corresponding to the 35 μm thick membrane, for two different residence times. As can be seen, a developed concentration profile forms near the channel entrance even at the highest operated flow velocity. This is due to the relatively fast transverse diffusion compare to the convection transport in x direction in our microfluidic channel. By comparing the two timescales for transport in normal ($\perp$ diffusion) and tangential ($\parallel$ convection) direction (Eq.(8)), we obtained a ratio ranging from 0.096 to 0.96. As demonstrated in Figure 4.5 (b), where Re is 0.084, the normal diffusion results in a nearly constant concentration gradient along the y direction. For such cases, the simplified 1D model accurately describes the performance of the PV process.

To accomplish a quantitative optimisation of the system performance, the separation efficiency can be predicted in terms of the factor Hk_m/D (Fig. 4.6, for a fixed value of channel height H). This factor sets

Figure 4.5: Local concentration profiles for $k_m = 4.94 \cdot 10^{-7} \text{ms}^{-1}$ ($35 \mu\text{m}$ membrane). (a) Residence time = 26 s, $\text{Re}=0.84$. (b) Residence time = 265 s, $\text{Re}=0.084$. The white curves indicate the boundary between the bulk ($c_{\text{bulk}} \geq 99\%c_0$) solution and the depletion zone.

Figure 4.6: Dependence of acetone removal efficiency on the performance factor Hk_m/D . Symbols represent the experimental results and lines correspond to the simulations. m represents the symbol for the slope of the curves.

the boundary flux (as in Eq.(5)) normalised by the diffusive flux. For each residence time, an increase in this ratio, which is an increase in k_m here, enhances the removal efficiency. When membrane transport is limiting, any increase in k_m will result in a proportional increase in removal efficiency,

giving a slope equal to 1. As can be seen, the obtained slopes vary from ~ 1 to < 1 with increasing k_m values. The symbols in Fig. 4.6 indicate the performance of our micro-PV experiments (the gray region), which is at the transition towards the rate limiting regimes. Such findings allow us to identify whether mass transport in the fluid phase or in the membrane is rate limiting and the extend of improvement that can be obtained.

4.5 Conclusions

Implementing pervaporation into a microfluidic device is presented to study VOCs removal from aqueous mixtures. An acetone removal efficiency of 81% is achieved within just 3 minutes at room temperature by a $35\ \mu\text{m}$ thick PDMS membrane. The use of a microfluidic format drastically improves mass transport in the boundary layer, which provides adequate membrane performance assessment. The derived performance number, Hk_m/D , based on the intrinsic system parameters is capable in assisting process design for both micro-and macro-scales. Our microfluidic device shows promising potential as a universal tool for the removal of various VOCs by pervaporation.

Bibliography

- [1] Wörz O, Jäckel K, Richter T, Wolf A (2001) Microreactors, a new efficient tool for optimum reactor design. *Chem Eng Sci* 56:1029–1033.
- [2] Doku GN, Verboom W, Reinhoudt DN, van den Berg A (2005) On-microchip multiphase chemistry-a review of microreactor design principles and reagent contacting modes. *Tetrahedron* 61:2733–2742.
- [3] Hessel V, Renken A, Schouten JC (2006) *Handbook of Micro-Reactor Engineering and Chemistry* (Wiley-VCH).
- [4] Nguyen NT, Wu Z (2005) Micromixers-a review. *J Micromech Microeng* 15:R1–R16.
- [5] Hessel V, Löwe H, Schönfeld F (2005) Micromixers-a review on passive and active mixing principles. *Chem Eng Sci* 60:2479–2501.
- [6] Lam KF, Sorensen E, Gavriilidis A (2013) Review on gas–liquid separations in microchannel devices. *Chem Eng Res Des* 91:1941–1953.
- [7] Kenig EY, Su Y, Lautenschleger A, Chasanis P, Grünewald M (2013) Micro-separation of fluid systems: A state-of-the-art review. *Sep Purif Technol* 120:245–264.
- [8] Hartman RL, Jensen KF (2009) Microchemical systems for continuous-flow synthesis. *Lab on a chip* 9:2495–2507.
- [9] Hartman RL, Naber JR, Buchwald SL, Jensen KF (2010) Multistep microchemical synthesis enabled by microfluidic distillation. *Angew Chem Int Ed Engl* 49:899–903.

- [10] Broyles BS, Jacobson SC, Ramsey JM, Chromatogr HMJ (2003) Sample Filtration , Concentration , and Separation Integrated on Microfluidic Devices . *Anal Chem* 75:2761–2767.
- [11] Webb D, Jamison TF (2010) Continuous flow multi-step organic synthesis. *Chem Sci* 1:675.
- [12] Chan T, Priestman G, MacInnes J, Allen R (2008) Development of a micro-channel contactor–separator for immiscible liquids. *Chem Eng Res Des* 86:65–74.
- [13] Scheiff F, Mendorf M, Agar D, Reis N, Mackley M (2011) The separation of immiscible liquid slugs within plastic microchannels using a metallic hydrophilic sidestream. *Lab Chip* 11:1022–1029.
- [14] Zhang Y, Kato S, Anazawa T (2010) Vacuum membrane distillation by microchip with temperature gradient. *Lab Chip* 10:899–908.
- [15] Kaufman Y, Kasher R, Freger V (2012) Microfluidic NF/RO separation: Cell design, performance and application. *J Membr Sci* 396:67–73.
- [16] Smitha B, Suhanya D, Sridhar S, Ramakrishna M (2004) Separation of organic-organic mixtures by pervaporation-a review. *J Membr Sci* 241:1–21.
- [17] Feng X, Huang RY (1997) Liquid Separation by Membrane Pervaporation : A Review. *Ing Eng Chem Res* 36:1048–1066.
- [18] Jiang JS, Vane LM, Sikdar SK (1997) Recovery of VOCs from surfactant solutions by pervaporation. *J Membr Sci* 136:233–247.
- [19] Ulrich B, Frank TC, McCormick A, Cussler E (2014) Membrane-assisted voc removal from aqueous acrylic latex. *J Membr Sci* 452:426–432.
- [20] Ramprasad S, Palmer JD (2007) A Silicon Microseparator based Pervaporation Process for Separation of Ethanol/Water Mixtures using a Polymer Membrane. *Sep Sci Technol* 42:2483–2499.
- [21] Leng J, Lonetti B, Tabeling P (2006) Micro-evaporators for kinetic exploration of phase diagrams. *Phys Rev Lett* 96:084503.

- [22] Camou S, Shimizu A, Horiuchi T, Haga T (2009) Selective aqueous benzene detection at ppb level with portable sensor based on pervaporation extraction and UV-spectroscopy. *Procedia Chem* 1:1495–1498.
- [23] Ziemecka I, Haut B, Scheid B (2015) Hydrogen peroxide concentration by pervaporation of a ternary liquid solution in microfluidics. *Lab Chip* 15:504–511.
- [24] Daubersies L, Leng J, Salmon JB (2013) Steady and out-of-equilibrium phase diagram of a complex fluid at the nanolitre scale: combining microevaporation, confocal Raman imaging and small angle X-ray scattering. *Lab Chip* 13:910–9.
- [25] Schindler M, Ajdari A (2009) Modeling phase behavior for quantifying micro-pervaporation experiments. *Eur Phys J E Soft Matter* 28:27–45.
- [26] Lipnizki F, Trägårdh G (2001) Modelling of Pervaporation: Models To Analyze and Predict the Mass Transport in Pervaporation. *Sep Purif Methods* 30:49–125.
- [27] Karlsson HO, Trägårdh G (1993) Pervaporation of dilute organic-waters mixtures. A literature review on modelling studies and applications to aroma compound recovery. *J Membr Sci* 76:121–146.
- [28] Noworyta A, Kubasiewicz-Ponitka M, Koziol A (2011) Mass and heat transport resistance in pervaporation process. *Desalin Water Treat* 26:226–235.
- [29] Cussler EL (2009) *Diffusion: mass transfer in fluid systems* (Cambridge university press).
- [30] Côté P, Lipski C (1990) Reducing concentration polarization in pervaporation for trace contaminant removal. *Proc 1990 Int Cong Memb Memb Proc, Chicago* :325.
- [31] Lipski C, Côté PL (1990) The use of pervaporation for the removal of organic contaminants from water. *Environ Prog* 9:254–261.
- [32] Squires TM, Messinger RJ, Manalis SR (2008) Making it stick: convection, reaction and diffusion in surface-based biosensors. *Nat Biotechnol* 26:417–426.

- [33] Wijmans JG, et al. (1996) The role of boundary layers in the removal of volatile organic compounds from water by pervaporation. *J Membr Sci* 109:135–146.
- [34] Li L, Xiao Z, Tan S, Pu L, Zhang Z (2004) Composite PDMS membrane with high flux for the separation of organics from water by pervaporation. *J Membr Sci* 243:177–187.
- [35] Blume I, Wijmans JG, Baker RW (1990) The separation of dissolved organics from water by pervaporation. *J Membr Sci* 49:253–286.
- [36] Hollein M, Hammond M, Slater C (1993) Concentration of dilute acetone-water solutions using pervaporation. *Sep Sci Technol* 28:1043–1061.
- [37] Nijhuis HH (1990) *Removal of trace organics from water by pervaporation: a technical and economic analysis*. Ph.D. thesis, University of Twente.
- [38] Aran K, Sasso LA, Kamdar N, Zahn JD (2010) Irreversible, direct bonding of nanoporous polymer membranes to pdms or glass microdevices. *Lab Chip* 10:548–52.
- [39] Liu SX, Peng M (2005) Verification of mass transfer simulation with CFD using highly accurate solutions. *Comput Electron Agric* 49:309–314.
- [40] Lopes JP, Cardoso SS, Rodrigues AE (2011) Criteria for kinetic and mass transfer control in a microchannel reactor with an isothermal first-order wall reaction. *Chem Eng J* 176:3–13.
- [41] Urtiaga A, Gorri E, Beasley J, Ortiz I (1999) Mass transfer analysis of the pervaporative separation of chloroform from aqueous solutions in hollow fiber devices. *J Membr Sci* 156:275–291.

Visualization and Characterization of Interfacial Polymerization Film Formation

W^E present a microfluidic platform to visualize the formation of free-standing films by interfacial polymerization. A microfluidic device is fabricated, with an array of micropillars to stabilize an aqueous-organic interface that allows a direct observation of the films formation process via optical microscopy. Both non-fluorescent and fluorescent amines were introduced in this work to study the formation kinetics. For the non-fluorescent experiments, three different amines are selected to react with trimesoyl chloride: piperazine, JEFFAMINE[®]D-230, and an ammonium functionalized polyhedral oligomeric silsesquioxane. Tracking the formation of the free-standing films in time reveals strong effects of the characteristics of the amine precursor on the morphological evolution of the films. A shift of reaction from aqueous phase to organic phase was occurred for JEFFAMINE[®]D-230 membranes. Introducing a fluorescent amine provides insights on the real-time kinetics by tracking the molecular consumption in the bulk solution. Our in-situ real-time observations provide information on the kinetics and the changing location of the polymerization. This provides insights with important implications for fine-tuning of interfacial polymerizations for various applications.

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5.1 Introduction

Interfacial polymerization (IP) is widely employed for the rapid production of high-selective polyamine (PA) films, and it finds intensive application in the fabrication of membranes for molecular separation [1, 2]. In IP the polymerization and the film formation occur simultaneously at the interface between two immiscible solvents. Typically, an amine is dissolved in an aqueous phase and an acyl chloride is dissolved in an organic phase. The increases in thickness and density of the film that is forming inhibit the diffusion of the monomers through, and force the polymerization reaction to be self-limiting. The IP film is generally fabricated atop a porous support, by impregnating this support with an aqueous amine solution followed by immersion in an organic phase. Film thicknesses range from a few nanometer to several micrometer, depending on the monomer types and concentrations, combination of solvents, additives, and reaction times [3–6].

The extensive application of IP films has commenced many attempts to correlate the formation kinetics to the film properties, in particular to the molecular separation performance [3, 7–10]. However, the extremely rapid kinetics, and potentially changing characteristics of the film formation process in time, complicate both computational and experimental studies. Enkelmann and Wegner [8] developed the very first model considering film formation to be dictated by concurrent diffusion and reaction limitations. Since then many other studies have been focused on interfacial polymerization, aiming at finding relations between film formation kinetics and film properties such as the film thickness, polymer weight and charge distribution [11–16]. An extensive review of such models is given by Berezkin [17]. The various models range from simple phenomenological approaches to detailed molecular dynamics. In the most recognized models the film formation is considered to be a multistage processes: firstly incipient film formation occurs, followed by a slow-down of the polymerization reaction to a fully diffusion limited film growth. These models are referred to as ‘double-layer model’, as the film formed by the multi-stage process consists of a selective dense layer atop by a more loose layer.

Experimental studies also have revealed that the physic-chemical properties of IP films vary with location inside the films [4, 7, 8, 18]. Quantitative prediction of these variations has proven to be complicated, and also generic film property-performance relations have not yet been estab-

lished. Despite that the occurrence of dual regions in IP films has also been observed frequently in experimental studies, a generic quantitative prediction of the properties of these regions remains to be challenging.

Several reviews can be found on experimental IP studies [1, 2, 19, 20]. These studies have not included in-situ analysis techniques that allow direct visualization of the film formation process, for validating the modeling work. Most film formation kinetics have been investigated by monitoring the reactant consumption and/or the film thickness in time, for various preparation conditions. Real-time IP film formation has mostly been investigated within the context of microencapsulation formation [4, 14, 21–23]. Yadav et al. [21] has succeeded in accessing the monomer consumption in the aqueous phase by employing an on-line pH probe. Chai et al. [4] has tracked the film thickness in time by using light reflection and pendant-drop tensiometry. They have confirmed that the kinetics of their process were diffusion-controlled. These techniques have limitations in the assessment of the formation process of supported and/or free-standing IP films. In addition to the kinetics of film formation, the film properties are expected to be affected by the location of the reaction. Generally the reaction is thought to occur in the organic phase, due to the rapid hydrolysis of acid chloride in water and the asymmetric solubility of the reactants between both phases [7, 23, 24]. Scanty experimental real-time observations of the location of film formation have been revealed due to the lack of in-situ techniques. Observations of penetration of the IP film into the porous support imply that the reaction can occur in the aqueous phase [25, 26].

Besides, fluorescence microscopy is an alternative tool for tracking and imaging the in-site formation of IP films. By introducing a fluorescent reactant in either organic or aqueous phase, the insights of the formation kinetics can be accomplished by monitoring the intensity change in time, which can be calibrated to a concentration change. In general, the concentration is linearly related to the fluorescence intensity in a diluted solution range ($c < 10^{-3}$ mol L⁻¹ [27]).

Here we attempt to establish a system that enables to track the kinetics of free-standing IP film formation, and to visualize the reaction location. Such a system can be used to address these questions by employing a microfluidic platform. The design of the microchips comprises an array of pillars inside the microchannels, allowing adequate stabilization of the aqueous-organic interface. The controlled stabilization of the

liquid-liquid interface at designated position enables visualizing the film formation process in-situ, providing information on the evolution of the kinetics and the location of the polymerization reaction.

We have conducted two methodologies in this study. In the first method, we have investigated the influence of different amine monomers on both formation kinetic and locations. In the second method, we have introduced a fluorescent amine 4,4,-diamino-2,2-stilbenedisulfonic acid (DASSA) into the aqueous phase. The consumption rate of DASSA can be accomplished by capturing its fluorescent intensity drop in time. Therefore, the formation kinetics of IP films in real-time can be monitored.

Figure 5.1: (A) Silicon-Glass bonded microchip for IP membrane formation. (B) White light interferometer image of a 3D microfluidic configuration 1 with hexagon-shaped subchannel. (C) Optical microscopy image of a stable gas-aqueous interface control by configuration 1. (D) Optical microscopy image of a stable organic-aqueous interface control at a zigzag-shaped subchannel in configuration 2.

5.2 Experimental

5.2.1 Microchips

The microchannels were fabricated on a silicon wafer by standard photolithography followed with deep reactive ion etching. The silicon wafer was anodically bonded to a glass wafer (Fig. 5.1(A)). The bonded chip

was enclosed to a tailor-made chip holder and connected (Upchurch connections) to elevated reservoirs for flow control.

5.2.2 Interfacial polymerization membrane formation

Before the interfacial polymerization reaction, the inner walls of the microchannels were chemically hydrophobized by silicon oil (20 cSt, Sigma-Aldrich) [28]. Three amine solutions were prepared at 0.5 wt% in deionized water: piperazine (PIP, Sigma-Aldrich), JEFFAMINE®D-230 (JEFF, Huntsman), and a hybrid polyhedral oligomeric silsesquioxane (POSS, Hybrid Plastics). Sodium hydroxide (Sigma-Aldrich) was added to the ammonium functionalized POSS solution [29]. An amine solution was introduced into one of the main channels by providing a hydrostatic pressure of 2400 Pa ($\Delta h=240$ mm). The micropillars provided adequate pinning sites to stabilize the G-L interface (Fig. 5.1(C)). After the G-L interface was stable, the outlet of the aqueous solution was blocked to equalize the pressure in the microchannel and create a stationary aqueous-G interface. Upon that, a trimesoyl chloride (TMC, Sigma-Aldrich) in hexane solution (0.25 wt%, Sigma-Aldrich) was flowed into the adjacent channel by another hydrostatic head. The offered pressure ($\Delta h=100$ mm) was just sufficient to drive in the organic solution to minimize the caused instability on the formed L-L interface. Once the interface was formed, the reaction was ensured to occur under a free-pressure-driven condition by opening all the connections to the air. The IP film formation was recorded using a high-speed camera (AxioCam MRc 5, Carl-Zeiss) connected to the optical microscope (Axiovert 40, Carl-Zeiss). Pure water and hexane were flowed into the corresponding channels to remove unreacted monomers after the formation process was completed.

5.2.3 Scanning Electron Microscope (SEM)

We employed two methods to prepare SEM samples regarding the film properties. Samples of PIP and JEFF films were prepared by dissolving the covered glass slide in 50% HF acid for 70 min under an etching rate of $7 \mu\text{m min}^{-1}$. Thermal bonded devices (see S.I.A) could be separated by mechanical force, after the POSS film formation. The prepared samples were firstly dried in a nitrogen box for overnight and then sputtered with a thin gold film (~ 30 nm). Both surface and cross-section of the films were

visualized by SEM (JOEL JSM-5600LV) at 5 kV under magnifications from x2000 to x18,000.

5.2.4 Water permeation measurements

The water permeability of the POSS-TMC film was analyzed by providing a constant feed pressure using hydrostatic heads. Hexane and DI water were firstly flowed into the main channel synchronously. The outlet of the water stream was blocked to equalize the pressure in the water-filled channel. The inlet and outlet of the hexane filled channel were opened to the atmosphere. A hydrostatic pressure difference of 3500 Pa ($\Delta h=350$ mm) was applied to the water stream. Permeating water droplets in the hexane phase were recorded by a camera. The droplet sizes were analyzed using the program ImageJ (Version 1.46). The water permeability was calculated from the change in droplet dimensions.

5.2.5 Tracking the formation kinetics by introducing fluorescent amine

The film was formed in the same method as described in section 3.2.2 by using chip displayed in Fig. 5.1(D). The prepared aqueous solution contains 0.18 wt% DASSA with 0.01 mol L^{-1} NaOH. The membrane formation process was visualized by a fluorescent microscope (Zeiss Axiovert A1 inverted microscope) and recorded by a fluorescent camera (Zeiss Axiocam Color 105). A HBO100 lamp (Carl Zeiss) was used as the excitation light source. The excitation filter has a wavelength of $360 \pm 40 \text{ nm}$ (ET360/40x-PF) and emission filter has a wavelength of 400 nm (FGL 400 nm) and the dichroic mirror was a 400 nm long pass filter (T4400lp). The camera was focused on a constant position among the pillar structure and the membrane formation process was recorded for approximately 400 seconds by a fluorescent camera (Zeiss Axiocam Color 105). Images were taken with a frame rate of approximately 2 fps with an exposure time of 234 ms. The intensity drop of the DASSA solution, perpendicularly from the membrane-aqueous interface to the aqueous bulk solution, was analysed by Matlab and converted into local concentration change by calibration beforehand.

A reference experiment regarding bleaching of DASSA in the aque-

ous phase was performed by using pure n-hexane as the organic solution. The intensity drop in time was recorded at an identical region as the reaction involved ones in the same time scale (400 s). Moreover, the release of acid during film formation process may interfere the intensity drop as well. We performed a measurement on intensity in time for various acidified DASSA solutions (0.18 wt%) using the same chip. The solutions were prepared as pH=6 (initial), pH=5 and pH=4 using CO₂ and HCl as acidifiers, respectively. Their results on intensity drop were subtracted from the reaction ones to ensure the reaction as the only incentive.

5.3 Results and discussion

The design of our microfluidic devices features two parallel channels, allowing the simultaneous flows of an aqueous and an organic stream. An array of micropillars (Fig. 5.1(A) and (B)) stabilizes the interface between the liquids, and provides mechanical support for the film that is formed at this interface. We have designed various pillar structures to optimize the L-L interface control and investigate their influences on the film formation process (see SI.A). The zigzag-located pillar (configuration 1, Fig. 5.1(C)) and the hexagon-shaped pillar (Configuration 2, Fig. 5.1(D)) provide well-stabilized interfaces and have been selected for this study. Configuration 1 offers the largest interfacial areas, which facilitates the microscopic observation. Configuration 2 was utilized for water permeation measurements as this configuration reduces the coalescence of growing water droplets. The fluorescent IP films were formed in configuration 2 as this configuration facilitates the intensity measurements.

We selected three different amines to react with TMC: PIP, JEFF and POSS. PIP is one of the most widely used aliphatic amines for the fabrication of nanofiltration and reverse osmosis membranes by IP. Its derived IP films typically exhibit a large free volume and pore size, enabling a high permeability [10, 30]. JEFF is a polyetheramine with long and flexible aliphatic chains. It has been scarcely selected as an amine candidate for IP film formation, due to the long flexible alkyl chains that result in an even larger free volume as compared to PIP. Films with a very open structure generally exhibit low salt retentions. POSS has recently drawn tremendous attention due to its unique hybrid structure. Supported POSS membranes exhibit an extremely dense morphology and thin thickness (<300

5.3. Results and discussion

nm) providing extraordinary performance for gas and liquid permeation applications [31, 32].

Figure 5.2(A) and (B) reveal the morphologies of films prepared with the two aliphatic amines. The reaction between PIP and TMC is fast, resulting in the formation of a $\sim 20 \mu\text{m}$ film in the hexane phase, within 30 s (Fig. 5.2(A2)). The direction of film growth implies that the reaction predominantly takes place in the organic phase. The optical microscopy image shows that the cross sectional morphology of the film does not vary strongly with axial position. The SEM micrograph of the film surface at the hexane side (Fig. 5.2(A3)) reveals some roughness. Such roughness has also been typically reported for IP formation of supported PIP films [10, 18]. Figure 5.2(B2) depicts a film obtained with JEFF as amine source. The film consists of a stack of two regions: a $\sim 5 \mu\text{m}$ dense region in between the pillars, and a more loose and irregular region up to $25 \mu\text{m}$ towards the organic phase. The SEM image (Fig. 5.2(B3)) confirms that surface of the film on the organic side is rougher as compared to the PIP derived film. It is noted that the thicknesses of the free-standing PIP and

Figure 5.2: IP film morphologies from the top-view of the microchannel formed by different aliphatic amines reacted with TMC. The left column shows the reaction schemes and the molecular weights (MW) of the corresponding monomers. The middle column are the microscopy images of the formed IP films in configuration 1. The right column are the SEM images of the corresponding micro-IP films.

JEFF films are up to ten times thicker than those of supported films. Similar differences between supported and free-standing films have also been

reported by others [4, 8]. The differences can be related to a more limited amount of amines available for the reaction in the case of an impregnated support, and mechanical stabilization of the liquid-liquid interface by the porous support.

Figure 5.3: Optical microscopy images of JEFF-TMC film formation process. (A) –(E) JEFF IP film formation at different time steps. (E) The JEFF IP film morphologies after drying the hexane phase. (A1)-(E1) Highlighted initial film morphologies and adjacent pillars. (B2)-(E2) Highlighted film-liquid interface in different time steps (Yellow: film/aqueous interface at $t=35$ s. Blue: film/organic interface at $t=112$ s. Black: film/aqueous interface after the reaction is complete).

Exploiting our microfluidic platform, the film formation process can be traced in time. Figure 3 reveals the evolution of film formation for the polymerization of JEFF with TMC. Initially, a thin JEFF film is formed instantly as the interface is generated (Fig. 5.3(A)). The positions of the initial interface and its adjacent three pillars are highlighted in red (Fig. 5.3(A1)-(E2)). The growth direction and thickness in time can be determined by measuring the deviation of the film/liquid interface from the initial interface (SI.2). At 35 s, a film has been formed with an average thickness of $\sim 2 \mu\text{m}$ in the aqueous phase (the film/aqueous interface is indicated in yellow), and a thickness of less than $1 \mu\text{m}$ in the organic phase (Fig. 5.3(B2)). Such growth implies that, initially, the polymeriza-

Figure 5.4: SEM images of membrane morphologies at both aqueous and hexane phase. (A) is jeffamine (jeff) - TMC membrane and (B) is POSS - TMC membrane.

tion reaction predominantly occurs in the aqueous phase, instead of in the organic phase. This is distinct from observations for PIP (Fig. SI(2)). The different initial behavior can be rationalized from the difference in distribution of the amines over the two liquid phases; the more hydrophilic JEFF has a lower tendency to go into the organic phase as compared to PIP. For JEFF, after 112 s the thickness of the film grown into the organic phase has increased to $\sim 3 \mu\text{m}$, while no apparent further growth into the aqueous phase is observed (Fig. 5.3(C2)). This indicates that the formed film possesses an increased mass transport resistance for TMC that localizes the reaction into the organic phase. Up to 112 s, the growth of the film has resulted in a homogenous thickness, and the film only grows perpendicularly from the incipient layer. Upon that, the JEFF film further grows into the hexane phase in more irregular fashion. After approximately 900 s no apparent further growth of the film is observed. Meanwhile, the reaction in the aqueous solution has proceeded at a low rate, as is manifested by a slight shift of the interface between films and aqueous solution (Fig. 5.3(E2)).

Differently from PIP and JEFF, POSS established a more homogeneous film in terms of thickness and morphology between adjacent pillars (Fig. 5.2(C2)). The obtained film thickness is thinner than 300 nm, which is approximately twice thicker than that of the supported analogue [29]. By

tracking the formation of POSS IP film in time, we observed no apparent growth of film thickness and density after 4 s (4 s was the minimal time step we used). We presume that the huge POSS molecule tends to form a dense film (Fig. 5.2(C3)), and the transport of POSS through the forming film is instantly obstructed. The reaction is unable to proceed in the water phase due to the hydrolysis of the acid chloride group of TMC. Therefore, the film formation is self-limited within such a short time. The POSS film is not only very thin, on both the organic and aqueous side of the membrane a very smooth surface is observed in the SEM images in Fig. 5.4 (B1) and (B2). In contrast, the JEFF derived film shows a slightly rougher surface on the aqueous side, and a very much rougher surface on the organic side. A similar correlation between film thickness and surface morphology, when comparing different amine monomers, has also been observed for supported membranes [10].

Compared to the morphologies of POSS and PIP films, the JEFF film shows a rougher surface in the hexane phase. The flexible aliphatic chain of JEFF molecular tends to form a film with an open, gel-like or high swollen structure. A lower reactivity of JEFF with TMC compared to that of PIP, can be assumed by correlating the reaction time to the formed film thickness (30 min for $\sim 20\ \mu\text{m}$). The swollen nature and slow formation process of the JEFF films could explain the rougher surface compared to PIP and POSS films [3].

Figure 5.5: Optical images of the POSS film for water permeation at different time steps.

We conducted a facile test to measure the water permeability of the free-standing POSS IP films. After around 1500 s a series of regular shaped water droplets are formed in the hexane phase (Fig. 5.5(A)) that continue to grow in time. The small variation in the size of the droplets indicates that the permeance of the film is similar at all locations in the array of pillars. From the change in the projected dimensions of the droplets their volume is calculated, assuming a spherical shape. The derivative of the volume with respect to time is converted to the water permeability, which is on the order of $10 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. This is about 30 times higher than that reported for the polyacrylonitrile (PAN) supported POSS films [29]. A relative lower water flux of IP films is obtained when a hydrophobic support is employed [33]. The absence of a hydrophobic PAN support as well as morphological differences, may cause the higher water permeability of the free-standing POSS film compared to those of the supported ones.

Figure 5.6 shows the formation process of DASSA IP films. At first, a stable aqueous-air interface was formed by filling the bottom channel with DASSA solution (Fig. 5.6(A)). After opening the valve to fill the upper channel with TMC solution, local high fluorescent intensity appeared at the interface (Fig. 5.6(B)). Such high intensity disappeared with entering of the organic solution (Fig. 5.6(C)). This phenomena might be caused by the volatile property of hexane. Hexane vapors may enter the channel before the solution and condense at the interface or around the channel wall. This causes a reflection of the DASSA solution at the interface and results in increased intensity. At the mean while, the reaction occurred instantaneously and thin films started to form (Fig. 5.6(D)). Although this high-intensity at the interface occurred for less than 0.5 s, the formation kinetic at this time interval cannot be accurately monitored. Thus, we only calculated the intensity after this time interval, which is set as $t=0$ s as indicated in Fig. 5.6(D). After 400 s reaction time, no variations in the location or intensity of the organic-aqueous interface was observed. This implies a completion of the rapid reaction between DASSA and TMC.

A Matlab script was used to process the captured images and quantify the local intensity. As show in Fig. 5.6(D), the film formation between the highlighted adjacent pillars were set as the region of interest. Hundred identical prarallel lines perpendicular from the interface to the bulk of the DASSA solution were drawn using a Matlab script for all images. The local intensity in time, which is correlated to local concentration, is calculated by averaging the intensity of each line for a time step of 5 s till 400 s total

Figure 5.6: Florescent images of the DASSA film formation at different time steps. (A) The initially formed DASSA-Air interface. (B) Appearing highlighted lines at the interface caused by the condensation of hexane vapor. (C) Disappearing of the reflection with entering of the TMC-hexane solution. (D) Formation of DASSA films at $t=0$ s (F) The completion of the reaction after 400.52s reaction time.

reaction time (Fig. 5.6(F)).

Figure 5.7(A) plots the normalized concentration (corrected for bleaching) in time at different distances from the interface. A concentration gradient from the interface to the bulk solution is observed. This indicates a rapid reaction occurred at the interface. The concentration at the bulk ($x=1$) shows a continuous drop till 400 s and a lower and relative constant concentration at the interface, indicating a gradually decreasing concentration gradient. As the reaction proceeds the resistance of the DASSA films increases, which hinders the diffusion of DASSA molecular through the formed film.

Moreover, we have studied the formation kinetics of DASSA films by quantifying the overall molecular consumption rate, R_{mol} (mol s^{-1}), based on the data from Fig. 5.7(A). By assuming a homogeneous concentration distribution along the depth of the microchannel, R_{mol} equals to the loss of DASSA concentration in the bulk (Eq.5.1),

$$R_{mol} = \frac{c_{bulk,t_2} - c_{bulk,t_1}}{t_2 - t_1} \cdot l \cdot w \cdot d \quad (5.1)$$

where l is the length of the bulk phase (in x-axis), $340 \mu\text{m}$, w is the measured width (parallel lines), $35 \mu\text{m}$ and d is the depth of the channel,

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50 μm .

Figure 5.7: (A) Concentration drop over time at different distances from the interface to the bulk. (B) Molar consumption rate based on the depletion of the bulk concentration (black curve) and the increase in the molar amount of DASSA in the film (blue curve).

Figure 5.7(B) plots the transient R_{mol} and the increase of DASSA molecules in the film as functions of the reaction time. R_{mol} shows a fast decrease in the first hundred seconds followed by an almost constant consumption rate, $\sim 1.0 \cdot 10^{-16} \text{ mol s}^{-1}$. Correspondingly, a fast increase in the total amount of DASSA in the film was observed for the first hundred seconds (blue curve). For longer reaction times, the growth becomes constant.

Figure 5.8: Fluorescent image (A1) and non-fluorescent image (A2) of DASSA films formed in configuration 2 during flushing of reactants (10min reaction). Fluorescent image (B1) and non-fluorescent image (B2) of DASSA films formed in configuration 1 after drying (25min reaction).

As a result of solidification of DASSA during the film formation, the fluorescent intensity of the films is lower than that of the DASSA

solution. Thus, it is unrealistic to monitor the growth of film thickness in-situ directly. DASSA films were formed for different reaction times and configurations. The captured images in both fluorescent and LED light environments are displayed in Figure 5.8. As can be seen, DASSA tends to form a homogeneous thin film with TMC, for reaction times till 25 min along different pillar configurations. This is comparable to POSS films but differently from that of PIP and JEFF films. We speculate this is ascribed to the charge groups presented on the DASSA molecule. These charged groups may repel other DASSA molecules during the formation process and result in a very thin film in short time.

5.4 Conclusion

In conclusion, our microfluidic device allows a direct visualization of the IP film formation process. Based on the results of non-fluorescent amines, the amine monomer is proved to play a decisive role in the resulting film morphologies. We observe three different scenarios of IP film formation processes. PIP exhibits a rapid reaction with TMC and the reaction only occurs in the organic phase. JEFF tends to form a film in both aqueous and organic phases. The POSS IP film is approximately 300 nm thin and the reaction is terminated within seconds. Additionally, introduction a fluorescent amine provides insights on the real-time kinetics by tracking the molecular consumption in the bulk solution. Due to the interface of optical effects at the interface, monitoring of the instantaneous film formation and concentration consumption at the interface are not reliable. The molecular consumption shows a steep increase within the first hundred seconds and then reaches a constant value.

Our in-situ real-time observations of the interfacial film formation generate information on the kinetics as well as on the evolution of the reaction location. This provides insights that may have import implications for sensible fine-tuning of interfacial polymerization for various applications.

Bibliography

- [1] Petersen RJ (1993) Composite reverse osmosis and nanofiltration membranes. *J Membr Sci* 83:81–150.
- [2] Cadotte JE, King RS, Majerle RJ, Petersen RJ (1981) Interfacial Synthesis in the Preparation of Reverse Osmosis Membranes. *J Macromol Sci, Part A: Pure Appl Chem* 15:727–755.
- [3] Jegal J, Min SG, Lee KH (2002) Factors affecting the interfacial polymerization of polyamide active layers for the formation of polyamide composite membranes. *J Appl Polym Sci* 86:2781–2787.
- [4] Chai GY, Krantz WB (1994) Formation and characterization of polyamide membranes via interfacial polymerization. *J Membr Sci* 93:175–192.
- [5] Kong C, Shintani T, Kamada T, Freger V, Tsuru T (2011) Co-solvent-mediated synthesis of thin polyamide membranes. *J Membr Sci* 384:10–16.
- [6] Shenoy R, Bowman CN (2012) Kinetics of interfacial radical polymerization initiated by a glucose-oxidase mediated redox system. *Biomaterials* 33:6909–14.
- [7] Morgan PW, Kwolek SL (1959) Interfacial Polycondensation. 11. Fundamentals of Polymer Formation. *J Poly Sci* XL:299–327.
- [8] V Enkelmann GW (1976) Mechanism of Interfacial Polycondensation and the Direct Synthesis of Stable Polyamide Membranes. *Makromol Chem* 177:3177–3189.

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- [9] Kim C, Kim J, Roh I, Kim J (2000) The changes of membrane performance with polyamide molecular structure in the reverse osmosis process. *J Membr Sci* 165:189–199.
- [10] Veríssimo S, Peinemann KV, Bordado J (2006) Influence of the diamine structure on the nanofiltration performance, surface morphology and surface charge of the composite polyamide membranes. *J Membr Sci* 279:266–275.
- [11] Ji J, Dickson JM, Childs RF, Mccarry BE (2000) Mathematical Model for the Formation of Thin-Film Composite Membranes by Interfacial Polymerization : Porous and Dense Films. *Macromolecules* 33:624–633.
- [12] Freger V, Srebnik S (2003) Mathematical model of charge and density distributions in interfacial polymerization of thin films. *J Appl Polym Sci* 88:1162–1169.
- [13] Freger V (2005) Kinetics of Film Formation by Interfacial. *Langmuir* 21:1884–1894.
- [14] Bouchemal K, Couenne F, Brianc S, Fessi H, Tayakout M (2006) Polyamides Nanocapsules : Modeling and Wall Thickness Estimation Estimation. *AIChE J* 52:2161–2170.
- [15] Nadler R, Srebnik S (2008) Molecular simulation of polyamide synthesis by interfacial polymerization. *J Membr Sci* 315:100–105.
- [16] Oizerovich-Honig R, Raim V, Srebnik S (2010) Simulation of thin film membranes formed by interfacial polymerization. *Langmuir* 26:299–306.
- [17] Berezkin AV, Khokhlov AR (2006) Mathematical Modeling of Interfacial Polycondensation. *J Polym Sci, Part B: Polym Phys* 44:18–20.
- [18] Freger V (2003) Nanoscale Heterogeneity of Polyamide Membranes Formed by Interfacial Polymerization. *Langmuir* 37:4791–4797.
- [19] Song Y, Sun P, Henry L, Sun B (2005) Mechanisms of structure and performance controlled thin film composite membrane formation via interfacial polymerization process. *J Membr Sci* 251:67–79.
- [20] Lau W, aF Ismail, Misdan N, Kassim M (2012) A recent progress in thin film composite membrane: A review. *Desalination* 287:190–199.

- [21] Yadav SK, Suresh AK, Khilar KC (1990) Microencapsulation in polyurea shell by interfacial polycondensation. *AIChE J* 36:431–438.
- [22] Karode SK, Kulkarni RSS, Suresh AKS, Mashelkar RA (1997) New insights into kinetics and thermodynamics of interfacial polymerization. *Chem EngSci* 52:3243–3255.
- [23] Dhumal S, Wagh S, Suresh a (2008) Interfacial polycondensation—Modeling of kinetics and film properties. *J Membr Sci* 325:758–771.
- [24] Sundet Sa (1993) Morphology of the rejecting surface of aromatic polyamide membranes for desalination. *J Membr Sci* 76:175–183.
- [25] Bartels CR, Kreuz KL, Wachtel A (1987) Structure-performance relationships of composite membranes: Porous support densification. *J Membr Sci* 32:291–312.
- [26] Bartels CR (1989) A surface science membranes investigation of composite membranes. *J Membr Sci* 45:225–245.
- [27] Guilbault GG (1990) *Practical fluorescence*, volume 3 (CRC Press).
- [28] Arayanarakool R, Shui L, van den Berg A, Eijkel JCT (2011) A new method of UV-patternable hydrophobization of micro- and nanofluidic networks. *Lab Chip* 11:4260–6.
- [29] Dalwani M, et al. (2012) Ultra-thin hybrid polyhedral silsesquioxane–polyamide films with potentially unlimited 2D dimensions. *J Mater Chem* 22:14835.
- [30] Yang F, Zhang S, Yang D, Jian X (2007) Preparation and characterization of polypiperazine amide/PPEsk hollow fiber composite nanofiltration membrane. *J Membr Sci* 301:85–92.
- [31] Raaijmakers MJT, et al. (2014) Sieving of hot gases by hyper-cross-linked nanoscale-hybrid membranes. *J Am Chem Soc* 136:330–5.
- [32] Chua ML, Shao L, Low BT, Xiao Y, Chung TS (2011) Polyetheramine–polyhedral oligomeric silsesquioxane or organic–inorganic hybrid membranes for CO₂/H₂ and CO₂/N₂ separation. *J Membr Sci* 385–386:40–48.

- [33] McCutcheon JR, Elimelech M (2008) Influence of membrane support layer hydrophobicity on water flux in osmotically driven membrane processes. *J Membr Sci* 318:458–466.

Summary and Outlook

THE interactions between liquids and solids on the microscale is of great relevance as a result of the high surface-to-volume ratio. The ability to precisely control and locate fluid interfaces enables a broad range of inquiries and applications. In this work, we generated controlled fluid interfaces to investigate interfacial transport and reaction processes with a focus on the i) the influence of heterogeneous surface wettabilities on fluid dynamics, ii) mass transport near a diffusive interface and iii) characterization of the reaction kinetics at an aqueous-organic interface.

6.1 Summary

Chapter 2 presents two distinct methods to selectively modify the surface wettability inside enclosed microchannels. We explored the mechanism of hydrophobization using silicon oil on glass substrates based on the protocol described by Arayanarakool [1]. The experimental results reveal that both UV illumination and temperature treatment enhance the resulting surface modification on glass. A faster immobilization and higher contact angle are obtained when the operating temperature is $\geq 60\text{ }^{\circ}\text{C}$, compared to that by UV irradiation process. $80\text{ }^{\circ}\text{C}$ treatment shows the highest reaction rate and resulting contact angles among all the processes, even without oxygen plasma pre-treatment. Such findings provide a simplified hydrophobization process in micro- and nanochannels compared to UV and plasma combined processes.

In another method, we propose an approach for spatial patterning of surface energy in a micro-capillary tube. Alternating hydrophilic/hydrophobic segments were obtained by combining photolithography with SAM chemistry. The method is highly reproducible and efficient as several capillaries can be treated simultaneously. The modified capillaries display a heterogeneous surface with very sharp boundaries between the hydrophilic and hydrophobic segments and excellent surface-uniformity. The smallest achieved dimension is $60\text{ }\mu\text{m}$. Our two-step method is versatile allowing to pattern multiple types of functional groups in discontinuous structures in an enclosed channel. Such structures are promising regarding the manipulation of segmented flows inside capillaries.

Chapter 3 evaluates the influence of heterogeneous surface wettability on altering the emulsion dynamics using a single co-flow microfluidic device. The oil-in-water emulsions were generated in a cylindrical glass capillary with a desired hydrophobic segment in the middle. The dynamics of the forming droplets in terms of morphology and motion are characterized by controlling the flow rates of both water and oil streams. Four scenarios of flow patterns, namely intact, adhesion, inversion and break-up, were observed when oil droplets passed from a hydrophilic surface to an adjacent hydrophobic one, depending on the flow velocity. By analyzing our experimental results, we found a critical convective time scale, Δt^* , which defines the regions for unchanged and changing emulsion dynamics. A fast moving droplet, which results in a relative thick and stable lubrication film with a life time $\Delta t < \Delta t^*$, stays intact in emulsion size and velocity when

passing the heterogeneous wetting surface. In contrast, droplets traveling with lower speeds result in a thinner lubrication film with a life time $\Delta t > \Delta t^*$, altering the emulsion dynamics in terms of adhesion, inversion or break-up. Corresponding to the Δt^* , we characterized a critical capillary number Ca^* to depict the dynamic transition as a function of velocity and emulsion size both experimentally and theoretically. Our results give insights on controlling dynamics of emulsions in microfluidics by means of flow velocity and heterogeneous wettabilities.

Chapter 4 presents a performance study on the removal of trace amount of acetone from water via pervaporation in a microdevice to provide insight on mass transport limitations. The mass transport of acetone from the liquid channel to the polydimethylsiloxane (PDMS) membrane is investigated both experimentally and numerically. The mass transfer coefficients of acetone through the liquid boundary layer (k_l) and the membrane (k_m) are quantitatively investigated and compared using 1- and 2D numerical models. High acetone removal efficiency of 81% is achieved for just 3 minutes residence time at room temperature for a 35 μm thin membrane. The results reveals a fully developed concentration profile in the liquid channel. The mass transfer coefficient k_l is 10-100 times larger than k_m , demonstrating the advantages implementing pervaporation in microfluidics. The significance of concentration polarization can be neglected in our microfluidic device by comparing the ratio of timescales for diffusion in the normal ($\perp$) and advection in the tangential ($\parallel$) direction. The derived performance number, Hk_m/D , based on the intrinsic system parameters is capable in assisting process design for both micro- and macro-scales. Our microfluidic device shows promising potential as a universal tool for the removal of various VOCs by pervaporation.

Chapter 5 demonstrates a microfluidic system that enables to track the formation of free-standing films by interfacial polymerization and provides insight on the reaction kinetics. The fabricated microdevice, with an array of micropillars is capable of stabilizing an aqueous-organic interface that allows a direct visualization and characterization of the film formation process. We selected both non-fluorescent and fluorescent amines to characterize the formation kinetics for distinct chemistries. For the non-fluorescent experiments, three different amines are selected to react with trimesoyl chloride (TMC): piperazine, JEFFAMINE[®]D-230, and an ammonium functionalized polyhedral oligomeric silsesquioxane (POSS). The results reveal strong effects of the amine precursor characteristics on the

morphological evolution of the films. Piperazine exhibits a rapid reaction with trimesoyl chloride, forming a film up to 20 μm thick within half a minute. JEFFAMINE[®]D-230 displays much slower film formation kinetics. The location of the polymerization reaction was initially in the aqueous phase and then shifted into the organic phase. The POSS IP film is approximately 300 nm thin and the reaction is terminated within seconds.

For the fluorescent experiments, the selected fluorescent amine, 4,4'-diamino-2,2'-stilbenedisulphonic acid (DASSA), tends to form a homogeneous thin film with TMC, for reaction times till 25 min. Due to optical effects at the interface, monitoring of the instantaneous film formation and concentration profiles near the interface are not reliable. The molecular consumption in the bulk phase was characterized. The molecular consumption shows a steep increase within the first hundred seconds and then reaches a more constant value.

Our in-situ real-time observations of the interfacial film formation generate information on the kinetics as well as on the evolution of the reaction location. This provides insights that may have important implications for sensible fine-tuning of interfacial polymerization for various applications.

6.2 Outlook

6.2.1 Functionalizing micro-separator by integrating membrane technology

Including membrane technology into microfluidic devices provides a promising model for applications including contacting, separation and reaction. The presence of a membrane enables a stable interface for gas-liquid or liquid-liquid systems. In particular, a free-standing membrane presents a vertical-barrier between two phases, allowing a real-time visualization and characterization of the system performance from both sides, especially when fluorescent labeling chemicals are introduced. These characteristics facilitate the investigation on fluids transport across a selective interface for both applied and fundamental studies. Examples include the investigation on local concentration profiles near a semipermeable membrane via osmosis-driven flows [2], the local crystallization and evolution of a

chemical gradient under diffusiophoresis [3, 4] quantifying the diffusion coefficients in a binary system [5].

As demonstrated in Chapter 5, the formed free-standing POSS membrane is highly permeable for water but barely for n-hexane. The measured water permeability is about 30 times higher than that reported for the polyacrylonitrile (PAN) supported POSS membranes. This makes it promising to develop an IP membrane integrated micro-separator to separate aqueous-organic phases efficiently.

However, the in-situ formed IP membranes exhibits weak adhesion to the channel wall. Strengthening the membrane attachment is essential to prolong the device lifetime. Using a coupling agent, such as (3-aminopropyl)triethoxysilane (APTES), provides a covalent bond between the membrane and the channel wall [6]. The amine group of APTES is expected to react with carboxyl group of the polyamine film and the ethoxysilane group can react with surface hydroxyl groups.

Our preliminary results demonstrate that an experimental route combining hydrophobization, IP formation followed by APTES post-treatment is feasible to enhance the membrane-microdevice lifetime. The vapor induced hydrophobization process by chlorotrimethylsilane (CTMS) provides a sufficiently high contact angle for aqueous-organic interface control. This is essential for the formation of IP membranes inside microchannels (see Table 6.1). The APTES post-treatment after IP formation can effectively strengthen the formed membrane adhesion to the channel wall. Due to the lack of an in-situ characterization technique, we verified the concept by forming free-standing JEFF-TMC membranes in glass test tubes (see Fig.6.1). Detailed preliminary results are summarized in Appendix2.

The IP membranes are permeable to various solutes and solvents. We anticipate that the microdevices can generate a broad range of experimental capabilities to tune membrane formulas. For example, we prepared an IP membrane using a amine mixture of DASSA and JEFF, and the resulting membrane demonstrates excellent salt retention, 82% for NaCl and 97% for Na₂SO₄, respectively. Besides, this membrane also exhibits a relative homogeneous morphology compared to that of JEFF membranes. Integrating this membrane into a microdevice with strengthened adhesion can be promising.

Noticeably, the APTES post-treatment modifies the membrane prop-

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Table 6.1: Dynamic contact angle measurements on silicon slides under different modification processes.

Contact angle ($^{\circ}$)	$\theta_a(^{\circ})$	$\theta_r(^{\circ})$	Hysteresis
CTMS (G)	97.8 ± 6.5	75.6 ± 4.3	22.2
APTES (L)	75.5 ± 4.5	39.2 ± 7.0	36.3
CTMS (G) + APTES (L)	87.1 ± 7.2	61.6 ± 5.6	25.5
APTES (L) + CTMS (G)	82.0 ± 2.8	44.7 ± 4.4	37.3

The hydrophobization process was performed using CTMS via vapor deposition. Surface modification by APTES was conducted by immersing the substrates in APTES in ethanol solution (3 v/v%) at room temperature for 3 h. θ_a represents the advancing contact angle and θ_r represents the receding contact angle.

Figure 6.1: Adhesion test of free-standing IP membranes onto glass test tube in different conditions. (A) JEFF membrane formation in an CTMS pre-modified test tube. (B) JEFF membrane formation in a CTMS pre-modified test tube with an APTES post-treatment.

erties in terms of morphologies, water flux and salt retention (see Fig. 6.2). This allows to reconfigure the membrane properties after the IP process.

Figure 6.2: (a) The morphologies of formed JEFF-TMC membranes before and after APTES post-treatment. (b) Water permeability of the APTES modified JEFF membrane in a microchannel as a function of pressure. (c) Water permeabilities of supported JEFF membranes before and after APTES modification.

6.2.2 Effect of ionic strength on charged IP membranes

The fixed charge groups in the IP membrane matrix play an important role in aqueous ion transport. It influences the internal electrostatic charge within the membrane and rejection of charged species at the membrane surface [7, 8]. Various studies have been performed on investigating the effect of fixed charge and ionic strength on the resulting membrane performance in terms of water permeability and salt retention [9–11]. However, their influence on the resulting membrane thicknesses is scarcely reported. The reason may be attributed to the nature of the preparation method of the supported IP membrane, which often leads to a thickness $< 1\mu\text{m}$ regardless of the chemistry. As demonstrated in chapter 5, free-standing membranes prepared by JEFF and PIP exhibit thicknesses $> 20\mu\text{m}$, which is around 20 times thicker than their supported analogies. In contrast, free-standing POSS and DASSA films display thicknesses $< 1\mu\text{m}$, which is similar to their supported analogies. This suggests that amines with fixed charge groups result in thinner membranes. The presence of charge groups in the membrane matrix may result in charge neutralization at the membrane surface and electric double layer compression, giving a compacted free-standing membranes [11]. These findings aroused our interest to un-

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derstand the charge effects, or ionic strength on IP membrane morphology and performance, particularly for free-standing analogies.

We first investigated the charge effects using supported DASSA membranes. We amplified the charge influence on membrane performance and morphology by increasing the ionic strength of the amine solution before membrane preparation. Some of our preliminary results shown in Fig. 6.3 and Table 6.2 demonstrate a strong influence of ionic strength on the DASSA membrane performance. A higher ionic strength results in a membrane with higher water permeability and lower salt retention. A lower pH, on the other hand, results in a membrane with increased water permeability and salt retention (NaCl). It seems that adding salt interfered the charge neutralization in the membrane and lead to a less compressed membrane. Since DASSA contains sulfonic acid groups that provide a negatively charged membrane surface, a lower pH may shield the fixed charge group in the membrane giving a decreased salt retention. However, our results shows the opposite. We cannot express the reason currently. More efforts are suggested to study the mechanisms, such as zeta potential and SEM measurements.

Figure 6.3: The influence of ionic strength on membrane permeability

Table 6.2: Salt retentions of the supported DASSA membranes prepared in different conditions

Membrane	NaCl (2g/L, %)	Na ₂ SO ₄ (2g/L, %)
pH=6.5, no salt	82.0	97.4
pH=10.5, no salt	75.5	87.4
pH=6.5, 1M NaCl	78.4	97.6
pH=10.6, 1M NaCl	62.3	53.2
pH=10.6, 1M Na ₂ SO ₄	81.0	No retention

6.3 Samenvatting

Hoofdstuk 2 presenteert twee verschillende methoden voor de selectieve modificatie van de oppervlaktebevochtiging in gesloten microkanalen. Wij onderzochten het mechanisme van hydrofobisering met siliconenolie op glazen substraten gebaseerd op het protocol zoals beschreven door Arayanarakool [1]. De experimentele resultaten laten zien dat zowel belichting met UV als een temperatuursbehandeling de oppervlaktemodificatie van het glas verbeteren. Vergeleken met de resultaten die worden verkregen met het UV-belichtingsproces worden een snellere immobilisatie en grotere contacthoeken verkregen als de gebruikte temperatuur groter is dan 60° . Een behandeling op 80° geeft de hoogste reactiesnelheden en de grootste resulterende contacthoeken van alle processen, zelfs zonder voorbehandeling met een zuurstofplasma. Deze resultaten leveren, vergeleken met processen die een UV- en plasmabehandeling combineren, een vereenvoudigde hydrofobisatiemethode in micro- en nanokanalen op. Daarnaast geven wij met een andere procedure een methode voor het ruimtelijk structureren van de oppervlakte-energie in een micro-capillair buisje. Door het combineren van fotolithografie en SAM-chemie werden alternerende hydrofiele en hydrofobe segmenten gecreëerd. De methode heeft een hoge reproduceerbaarheid en is zeer efficiënt, omdat meerdere capillairen tegelijkertijd behandeld kunnen worden. De gemodificeerde capillairen hebben een heterogeen oppervlak met zeer scherpe overgangen tussen de hydrofiele en hydrofobe segmenten en een uitstekende oppervlakte-uniformiteit. De kleinste behaalde grootte is $60\text{ }\mu\text{m}$. Onze twee-stapsmethode heeft een ruime toepasbaarheid, waarmee verschillende discontinue structuren van diverse typen functionele groepen in een gesloten kanaal aangebracht kunnen worden. Dergelijke structuren zijn veelbelovend wat betreft de manipulatie van gesegmenteerde stromingen in capillairen.

Hoofdstuk 3 bekijkt de invloed van een heterogene oppervlaktebevochtiging op het veranderen van de dynamica van emulsies door gebruik te maken van meestroom in een enkel microfluidisch kanaal. De olie-in-water emulsies zijn gegenereerd in een cilindrisch, glazen capillair met een gewenst hydrofoob segment in het midden. De dynamica van de gevormde druppels in termen van morfologie en beweging zijn gekarakteriseerd door het controleren van de stroomsnelheden van zowel water als olie. Vier scenario's wat betreft stromingspatronen, namelijk intact, adhesie, inversie en scheiding, werden waargenomen wanneer de oliedruppels de overgang

van een hydrofiel naar een aangrenzend hydrofoob oppervlak passeerden, afhankelijk van de stromingssnelheid. Door analyse van onze experimentele resultaten vonden wij een kritische convectieve tijdschaal, Δt^* , welke de gebieden definieert voor een constante en veranderende emulsiedynamiek. Een snel bewegende druppel, wat resulteert in een relatief dik en stabiele lubricatiefilm met een levensduur $\Delta t < \Delta t^*$, blijft intact wat betreft emulsiegrootte en snelheid wanneer het heterogeen bevochtigde oppervlak wordt gepasseerd. Druppels die zich daarentegen langzamer voortbewegen leiden tot een dunnere lubricatiefilm met een levensduur $\Delta t > \Delta t^*$, veranderen de dynamiek van de emulsie wat betreft adhesie, inversie of scheiding. Correspondierend met de kritische tijdschaal Δt^* hebben wij een kritisch capillairgetal Ca^* gedefinieerd om de dynamische overgang as functie van snelheid en emulsiegrootte zowel experimenteel als theoretisch weer te geven. Onze resultaten geven inzicht in de controle van de emulsiedynamiek in microfluidische systemen middels stroomsnelheden en heterogene bevochtiging.

Hoofdstuk 4 beschrijft een studie naar de werking van het verwijderen van kleine hoeveelheden aceton uit water door pervaporatie in een microfluidisch platform, om zo inzicht te geven in de limiteringen in massatransport. Het massatransport van aceton uit het vloeistofkanaal naar het polydimethylsiloxaanmembraan (PDMS-membraan) werd zowel experimenteel als numeriek onderzocht. De massaoverdrachtscoëfficiënten van aceton door de vloeistofgrenslaag (k_l) en het membraan (k_m) werden kwantitatief onderzocht en zijn vergeleken met één- en tweedimensionale modellen. Een hoge efficiëntie van 81% in het verwijderen van aceton werd behaald met slechts 3 minuten verblijftijd bij kamertemperatuur voor een μm dun membraan. De resultaten laten een volledig ontwikkeld concentratieprofiel in het vloeistofkanaal zien. De massaoverdrachtscoëfficiënt k_l is 10-100 maal groter dan k_m , wat de voordelen van de implementatie van pervaporatie in de microfluidica benadrukt. De invloed van concentratiepolarisatie kan worden genegeerd in ons microfluidisch systeem, zoals blijkt uit een vergelijking van de tijdschalen voor diffusie in de normale richting ($\perp$) en advection in de stromingsrichting ($\parallel$). Het afgeleide prestatiegetal, Hk_m/D , gebaseerd op de intrinsieke parameters van het systeem, is waardevol bij het ontwerpen van processen op zowel micro- als macroschaal. Ons microfluidische platform laat een veelbelovende potentie zien als een universele methode voor het verwijderen van verschillende VOC's middels pervaporatie.

Hoofdstuk 5 laat een microfluidisch systeem zien dat het mogelijk maakt om de vorming van vrijstaande filmen door grensvlakpolymerisatie (interfacial polymerization, IP) te volgen en dat inzicht geeft in de reactiekinetiek. Met de gefabriceerde microchip met een opeenvolgende rij van micropilaartjes is het mogelijk om een water-organisch grensvlak te stabiliseren, wat directe visualisatie en karakterisering van het vormingsproces van de film mogelijk maakt. Wij selecteerden zowel niet-fluorescente als fluorescente aminen om de vormingskinetiek voor reacties met een verschillende chemie te karakteriseren. Voor de niet-fluorescente experimenten werden drie verschillende aminen geselecteerd voor de reactie met trimesoylchloride (TMC): piperazine, JEFFAMINE®D-230 en een met een ammoniumgroep gefunctionaliseerde polyedrisch-oligomerisch silsesquioxaan (POSS). De resultaten laten een sterk effect van de eigenschappen van de amineprecursor op de morfologische groei van de filmen zien. Piperazine vertoont een snelle reactie met trimesoylchloride, wat een film tot 20 μm dik vormt binnen een halve minuut. JEFFAMINE®D-230 laat een veel langzamere kinetiek in de vorming van de film zien. De locatie van de polymerisatiereactie was aanvankelijk in de waterige fase, maar verschoof vervolgens richting de organische fase. De POSS-IP-film is ongeveer 300 nm dik, en de reactie stopt binnen enkele seconden.

De voor de fluorescente experimenten geselecteerde fluorescente amine 4,4,-diamino-2,2,-stilbeendisulfonzuur (DASSA) neigt naar de vorming van een homogene dunne film met TMC voor reactietijden korter dan 25 minuten. Vanwege optische effecten aan het grensvlak was monitoring van de instantane filmformatie en van de concentratieprofielen niet betrouwbaar. De moleculaire consumptie in de bulkfase werd gekarakteriseerd. De moleculaire consumptie laat een sterke toename in de eerste honderd seconden zien en bereikt vervolgens een meer constante waarde.

Onze in-situ real time observaties van de vorming van grensvlakfilmen verschaft informatie over zowel de kinetiek als het verloop van de locatie van de reactie. Het inzicht dat dit oplevert kan belangrijke implicaties hebben voor de nauwkeurige afstemming van grensvlakpolymerisatie in verschillende toepassingen.

Bibliography

- [1] Arayanarakool R, Shui L, van den Berg A, Eijkel JC (2011) A new method of uv-patternable hydrophobization of micro-and nanofluidic networks. *Lab Chip* 11:4260–4266.
- [2] Jensen KH, Lee J, Bohr T, Bruus H (2009) Osmotically driven flows in microchannels separated by a semipermeable membrane. *Lab chip* 9:2093–2099.
- [3] Paustian JS, Azevedo RN, Lundin STB, Gilkey MJ, Squires TM (2013) Microfluidic microdialysis: Spatiotemporal control over solution microenvironments using integrated hydrogel membrane microwindows. *Phys Rev X* 3:041010.
- [4] Palacci J, Abécassis B, Cottin-Bizonne C, Ybert C, Bocquet L (2010) Colloidal motility and pattern formation under rectified diffusiophoresis. *Phys Rev Lett* 104:138302.
- [5] Vogus DR, Mansard V, Rapp MV, Squires TM (2015) Measuring concentration fields in microfluidic channels in situ with a fabry–perot interferometer. *Lab on a Chip* 15:1689–1696.
- [6] Owen MJ (2002) Coupling agents: chemical bonding at interfaces. *Adhes Sci Eng* 2:403–431.
- [7] Lee C, Hong J (1988) Characterization of electric charges in microporous membranes. *J Membr Sci* 39:79–88.
- [8] Fu P, Ruiz H, Thompson K, Spangenberg C (1994) Selecting membranes .

- [9] Elliott JE, Macdonald M, Nie J, Bowman CN (2004) Structure and swelling of poly (acrylic acid) hydrogels: effect of ph, ionic strength, and dilution on the crosslinked polymer structure. *Polymer* 45:1503–1510.
- [10] Xu Y, Lebrun RE (1999) Investigation of the solute separation by charged nanofiltration membrane: effect of ph, ionic strength and solute type. *J Membr Sci* 158:93–104.
- [11] Braghetta A, DiGiano FA, Ball WP (1997) Nanofiltration of natural organic matter: ph and ionic strength effects. *J Environ Eng* 123:628–641.

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Supplymentary information for Chapter 3

A.1 Microchips fabrication

Both anodic bonding and thermal bonding have been employed for the microchips fabrication in this work. The anodic bonding provides a strong and irreversible bonding strength for the microchips. The covered glass layer can be etched away by hydrofluoric acid solution (50%) for the SEM samples preparation. However, the decomposition of Si-O-Si bond in hydrofluoric acid make such method inapplicable for the SEM sampling of POSS-TMC films. Therefore, a thermal bonded chip was utilized for the POSS-TMC film formation and its SEM sample preparation. Such method creates sufficient bonding strength to accomplish the experiment of film formation and allows a mechanical separation of the chips afterwards. The microchips fabrication by both the anodic bonding and thermal bonding processes, including their recycling procedures are described here,

Anodic bonded chips

- Chips fabrication:
 1. Fabricating microchannel and vale holes on a silicon wafer (diameter =10 cm, thickness = 380 μm) by coupling the processes of standard photolithography with deep reactive ion etching.
 2. Cleaning both the glass and silicon wafers by immersing the wafers in 99% nitric acid for 20 min. Rinsing by DI water.

3. Pre-bond the glass and silicon wafers by placing the glass wafer above the silicon wafer.
 4. Anodic bonding by Anodic bonder EV-501.
 5. Dicing into single chips in the size of 2 cm x 1.5 cm.
 6. Hydrophobization and IP formation.
- SEM samples preparation.
 1. Seal the vale holes on the silicon slide by dicing foils.
 2. Etching away the glass slide by immersing the chip in hydrofluoric acid (50%) for 70 min. Rinsing by DI water.
 3. SEM imaging.
 - Recycling of the chips (without SEM sample preparation):
 1. Etching away the complete glass slide by immersing the chip in hydrofluoric acid (50%) for 80 min. Rinsing by DI water.
 2. Cleaning the survived silicon slides by immersing the slide in acetone for 1 h, piranha solution for 14 min, nitric acid (99%) for 20 min.
 3. Immerse silicon slides in Hydrofluoric acid (1%) for 30 s.
 4. Dicing a glass wafer into slides in the same size as the silicon slides.
 5. Cleaning the glass slides in 99% Nitric acid for 20 min
 6. Pre-bonding followed by anodic bonding.
 7. Hydrophobization.

Thermal bonded chips

- Chips fabrication:
 1. Fabricating the microchannels and vale holes on the silicon wafers (diameter=10 cm, thickness =380 μm) by coupling the standard photolithography with deep reactive ion etching.

2. Cleaning both the glass and silicon wafers by immersing the wafers in 99% nitric acid for 20 min. Rinsing by DI water.
 3. Pre-bond the glass and silicon wafers by placing the glass wafer above the silicon wafer.
 4. Placing the pre-bonded wafers in the furnace 400°C for 4 h.
 5. Dicing into single chips in the size of 2 cm x 1.5 cm.
 6. Hydrophobization and IP formation
- SEM samples preparation.
 1. Separating the chip by applying mechanical force on the bonding edge.
 2. SEM imaging the POSS-TMC films formed in the microchannel.
 - Recycling of the chips (without SEM sample preparation):
 1. Cleaning the opened slides by immersing them in acetone for 1 h, piranha solution for 14 min, nitric acid (99%) for 20 min.
 2. Immerse silicon slides in Hydrofluoric acid (1%) for 30 s.
 3. Pre-bonding followed by thermal bonding
 4. Hydrophobization and IP formation.

A.2 Interface control and pillar configurations

As described in the section 2.2, we attempted to create a stationary Aqu-Org interface for the IP films formation by the process controlling. As such, the formation process in terms of the reaction location and film growth rate were only reaction and diffusion controlled. On one hand, the organic phase was introduced into the channel by providing the lowest feeding pressure after a stationary Aqu-G interface was generated. On the other hand, all the connections were opened to atmosphere pressure the moment the Aqu-Org interface was formed. Once the reaction started, the Aqu-Org interface was replaced by Aqu-film-Org interfaces. As a result of the film adhesion onto the channel wall, the initial position of the formed

films can be localized till the end of the reaction, as indicated by the SEM images in Fig. A.1. The thickness of the film in time can be defined by the derivations of the L-film interfaces from this initial position.

Figure A.1: SEM images of the JEFF-TMC films formed in the adjacent pillars.

We have designed more than 40 types of pillar structures in terms of pillar shape and pillar distance to optimize the L-L interface control and investigate their influence on the formed film morphologies. Some of the configurations with successful IP film formations are shown in Fig. A.2(2)-(4). The pillar density (d , pillar length (horizontally) / pillar distance) is indicated in the images.

POSS

As can be seen, our designed pillar structures shows minor influence on the formed POSS film morphologies and thickness. POSS film establishes high homogeneities in terms of film thickness and morphology along all the pillar configurations (Fig. A.2). Observations of the film formation process can be problematic by the microscope when the pillar distance is shorter than $5\ \mu\text{m}$ ($d=2.5$). Square pillars (Fig. A.2, $d=1$) provides stable interface control. However, the cleaning flow after the reaction can easily break the films.

PIP

During the formation process, PIP displays fast kinetics with TMC, which instantly shifts the interface from the initial position into the hexane phase (Fig. A.3(A)-(D)). A $\sim 20\ \mu\text{m}$ thick film has been formed within 35 s and no growth in film density and thickness has been observed after that (Fig. A.3(A)-(B)). Such formation behavior implies a high preference of the formation location in the organic phase. The formed PIP-TMC films are highly independent on the pillar configurations since the reaction instantly drives the film formation into the organic phase, in most of the cases (Fig.

A.3). We have varied the PIP concentrations in water from 0.5 wt% to 2.5 wt%. The highest concentration of PIP solution drives the reaction into the organic phase the furthest and generates the thickest film. Only the lowest concentration can form films along the pillar-controlled interfaces.

Figure A.2: POSS-TMC film formation in different pillar configurations.

Figure A.3: PIP films formed in variety concentrations. (A)-(B) 0.5 wt%. (C) 2.5 wt%. (D) 1 wt%. (E) 0.5 wt%. (A)-(B) PIP-TMC film formation at different time steps. $d=1$ for all the pillar constructions..

JEFF

The formed JEFF-TMC film can be influenced by the pillar structures in some aspects (Fig. A.4). The appearance of the rough and irregular

A.3. Hexane permeability test by POSS-TMC films

morphologies shows in all the pillar structures. Multi-layer morphologies in the organic sides have been frequently observed(B).

Figure A.4: JEFF-TMC film formation in different pillar configurations.

A.3 Hexane permeability test by POSS-TMC films

The hexane permeability of POSS-TMC film has been tested in this study. We have firstly emptied the water-side channel by an air flow and then opened this channel to the atmosphere. After that, the other channel has been filled by hexane ($h=350$ mm) and its inlet and outlet have been blocked to maintain a certain pressure and prevent the evaporation of hexane. The system has been placed stationary for 17 h. We observed no difference in the hexane side channel but only a little wetting on the film-Air interface.

Figure A.5: Hexane permeability test by POSS-TMC film.