Separation dynamics of binary liquid mixtures -
Theory & Experiment

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ABSTRACT

Differences of wettability on chemically patterned surfaces allow to drive or guide liquid and even can be used to separate emulsions. It is conceivable to extend this concept to more complex systems like mixtures of multiple liquids, objects in liquids or mixtures of liquids with a higher degree of compatibility. But to do so it is necessary to understand which processes are relevant for separation and which parameters describe these processes. Using surfaces with an abrupt change of wettability and monodisperse Toluene- Water- mixtures as model emulsions we show that the separation process is a highly complex multiscale phenomena and present two theoretical approaches: On the one hand we consider the system to be a purely hydrodynamic system and transform differences of wettability into corresponding pressures. On the other hand we analyze the dynamics of single droplets. Comparing open and confined systems we find that the driving forces for separation are different.

Keywords: Fluid Transport, Flow, Fluidic Device Design, Micro Fluidic Devices, Fluidic Device Simulation

1 INTRODUCTION

In microfluidic systems differences of wettability on chemically patterned surfaces allow to drive liquid in the case of a surface energy gradient [1] and to guide liquid in case of abrupt surface energy change [2]. Recently our co-workers reported the possibility to separate emulsions on surfaces with surface energy gradients [3]. We study how chemically patterned surfaces can be applied for the separation of two incompatible liquids and introduce a novel simplified separation scheme utilizing surfaces with an abrupt change of surface energy. The separation of liquid mixtures induced by surface energy changes as a dynamic process involving (de-) wetting is a highly complex multiscale system. Especially with respect to the fact that the dynamics of single droplets on chemically patterned surfaces is still not fully understood and subject of current research [4]. We emphasize that in this case not phase separation like spinodal decomposition but emulsion separation induced by surface and interfacial tension is studied.
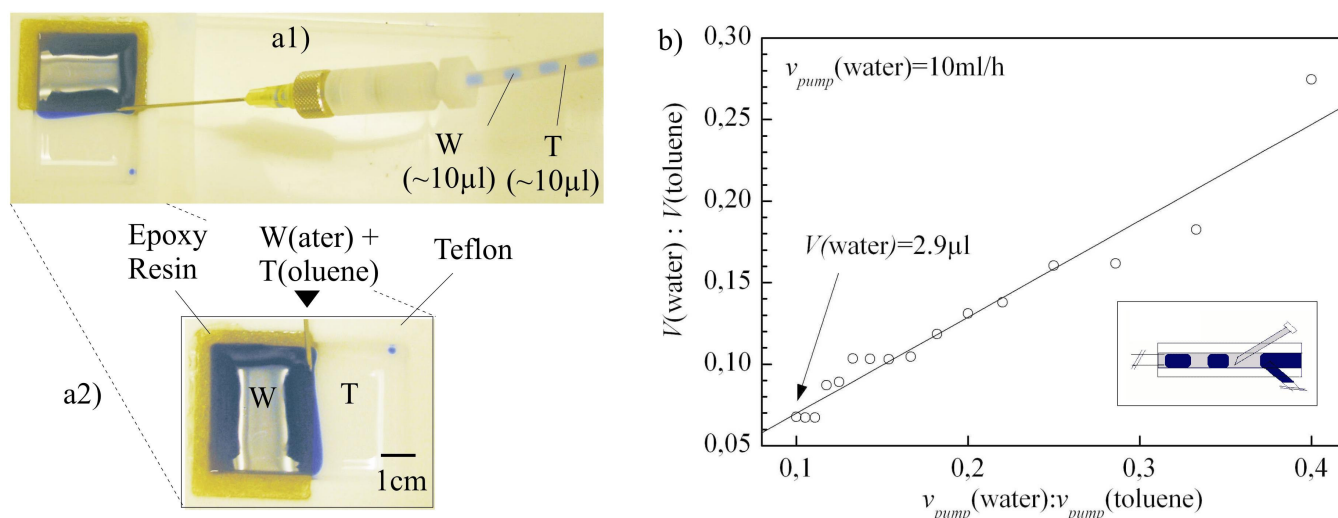

Figure 1: a) Separation of a water-toluene mixture in a microfluidic cell. b) Generation of monodisperse water-toluene-mixtures using a flow focusing geometry.
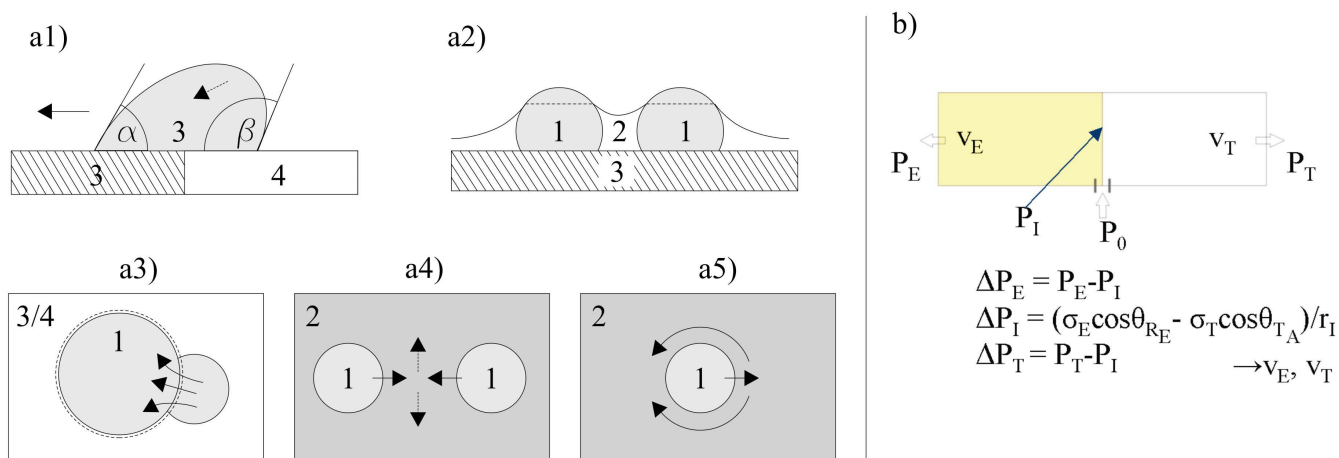
a1) a2) b)

α 3 β
3 4
1 2 1
3
3/4 1
2 1 1
2 1

P_E v_E v_T P_T
P_I P_0

$\Delta P_E = P_E - P_I$
$\Delta P_I = (\sigma_E \cos\theta_{R_E} - \sigma_T \cos\theta_{T_A})/r_I$
$\Delta P_T = P_T - P_I$
$\rightarrow v_E, v_T$

Figure 2: a) The separation process steps (1 = water, 2 = Toluene, 3 = hydrophilic surface, 4 = hydro-phobic surface): (a1) Laplace pressure difference induced water droplet movement to the hydrophilic surface. (a2) Water droplets coalescence due to capillary forces. (a3) The smaller drop emtpies into the bigger drop destabilizing the triple phase contact line and transferring kinetic energy. (a4, a5) flow of liquid 1 induces opposite flow of liquid 2 and vice versa . b) hydrodynamic model (grey- hydrophilic, white-hydrophobic): water only wets the hydrophilic side as long as the pressure at the interface is lower than a critical value ΔP_I.

2   RESULTS AND DISCUSSION

2.1   Monodisperse Emulsions

The separation is carried out on surfaces with an abrupt change of surface energy integrated into a separation cell using monodisperse emulsions produced by a self-constructed emulsion generator (**Fig. 1a,b**) to reduce the number of parameters which define the separation process. The emulsion generator consists of a liquid junction with two in- and one outlet. Each inlet is connected to a syringe pump filled with one of the two incompatible liquids. The syringe with the solvent (toluene) is connected to a metal needle which is injected into the Teflon pipe connected to the syringe filled with water. With such simple kind of a flow focusing geometry different pearl necklace like emulsions with controllable water to solvent volume ratios can be generated by varying the pumping speed (**Fig. 1b**). The minimum droplet volume is 2.9µl and limited by the tube diameter at the point of injection while the maximum droplet volume is given obviously by the total amount of liquid remaining in the corresponding syringe.

2.2   Separation of Binary Liquid Mixtures

The microfluidic separation cell is milled into a Teflon block (hydrophobic) with a cavity filled with epoxy resin (hydrophilic) (**Fig. 1a**). As emulsion we use Toluene/Water-mixtures where blue ink dissolved into the water is used to enhance the contrast. While the wetting of Toluene is just slightly influenced by hydrophilicity/ -phobicity water selectively wets the surfaces. The separation cell here is an open basin and separation continues to a certain extend even if both sides are completely wetted. The system is comparatively large so that gravitation forces play a role. Thus forces induced by surface tension difference are balanced by gravitational forces. Compared to a surface energy gradient [3] the abrupt change of surface energy enhances the surface induced liquid movement.

We analyze general aspects of the separation process on such surfaces and define the following fundamental process steps (**Fig. 2a**): (**a1**) When the liquid approaches the surface it is driven along the surface energy gradient. Though it may not be the only driving force it becomes plausible if one imagines a drop wetting a surface of varying surface energy. In this case the local contact angles would differ and go along with a corresponding change of the liquid surface curvatures. As a consequence the internal Laplace pressure would become different at different locations which causes liquid flow inside the droplet as long as the droplet boundaries are not pinned to the surface (a measure for the magnitude of such pinning energy is the contact angle hysteresis) and gravitational forces remain small. (**a2**) The separation process is enhanced by capillary bridges between liquid drops of the media with higher surface tension (e.g. water) formed by the liquid of lower surface tension (e.g. toluene). The capillary attraction is a long range interaction decaying exponentially with a characteristic interaction length in the order of millimeters called the capillary length. (**a3**) If two droplets merge the smaller droplet is emptying into the bigger droplet due to the higher internal Laplace pressure of the smaller droplet. The decrease in overall surface energy thus is transformed in kinetic energy directed along the pressure gradient. In most cases one drop is significantly larger which is the drop that results from previous separation processes and nearly consists of the total amount

of one type of liquid introduced into the system during separation. In contrast the second drop usually is a small liquid quantity introduced into the system short before coalescence. Thus droplet coalescence amplifies separation by transferring kinetic energy in the direction of the surface energy gradient. (**a4**, **a5**) A process slowing down separation is the fact that movement of one liquid causes liquid flow of the other. Here two processes can be distinguished: Firstly back flow in the opposite direction of liquid 2 induced by the movement of liquid 1 (**a5**). Secondly flow of liquid 2 induced by the coalescence of liquid drops 1 (**a4**). This situation corresponds to a competition between frictional forces and the previously described capillary attraction. It should be mentioned that contact angle hysteresis occurs in all cases and inhibits separation. The most important conclusion that can be drawn from the considerations above is that separation of incompatible liquid mixtures is not only possible if surface energy gradients are used but also if the surface energy changes in a stepwise manner as we demonstrate in this study.

2.3 Hydrodynamic Model

For applications of such systems the maximum volume rate characterizes the system performance. The latter of course will also depend on the volume ratios solvent to water. To investigate these effects we propose a hydrodynamic model (**Fig. 2b**) where surface tension differences are transformed into corresponding pressures. As the separation process is mainly driven by the selectivity of water one may firstly neglect the contribution of the solvent to this problem. In this model the separation cell consists of one hydrophobic tube (T=Teflon), one hydrophilic tube (E=Epoxy), an interface that withstands a certain pressure and an inlet vertical to the tubes at the interface. Water at pressure P_0 enters the surface, wets the hydrophilic side and flows out of the system at a pressure P_E with velocity v_E. At the interface a pressure P_I builds up. Due to contact angle hysteresis the interface can withstand a pressure ΔP_I given by the surface energies σ_E, σ_T ,the receding and advancing contact angles and the radius of curvature r_I at the interface. Once the pressure exceeds a certain level water will wet also the hydrophobic areas and flow through the second outlet at velocity v_T and pressure P_T. Due to the differences of ΔP_E, ΔP_T the velocities v_E , v_T which are parameters easy to determine should be different as well. Except σ_E, σ_T and P_0 all parameters are functions of y (for sufficiently large system dimensions variations in the x- direction can be neglected).

2.4 Droplet Coalescence

To shade a glance on the dynamics of merging droplets we use acid-base-indicator systems to visualize liquid flow (**Fig. 3a**). As acid-base-indicator reactions are much faster
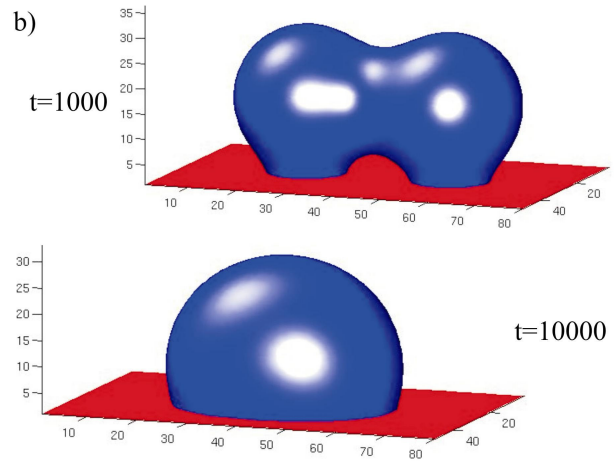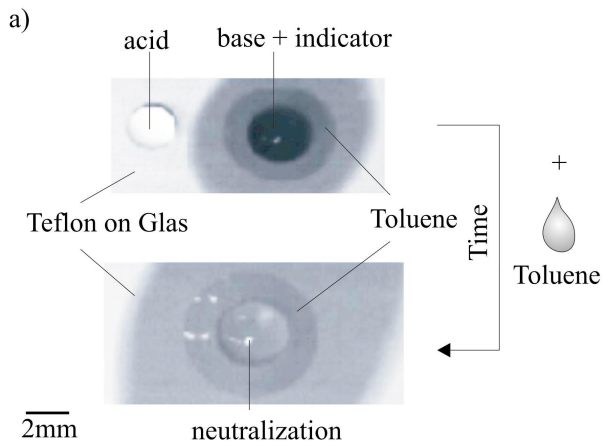

Figure 3: a) By adding a Toluene drop the acidic drop merges with the basic drop resulting in a neutral drop indicated by the colour change where the time scale is a measure for the kinetic energy available. b) LB Simulation of two droplets merging in the presence of a substrate (contact angle 110°). The presence of the substrates slows down the process.

a) open surface: $\Delta E \sim V^{2/3}$

b) confinement: $\Delta E \sim (d \cdot V)^{1/2}$

Figure 4: Reduction of the potential energy by the coalescence of two droplets.

than the liquid motion the color change of the liquid is an indicator for the kinetic energy of the liquid available to mix which depends on the droplet size. Complementary theoretical studies show that Lattice Boltzmann (LB) Simulations [5] enable to model relevant processes such as droplet coalescence on surfaces with the surface wettability as an input parameter (**Fig. 3b**). It is noteworthy that LB Simulations also may be used to visualize flow inside droplets. Scaling down device size will require to carry out separation inside a gap to prevent evaporation. Therefore we compare the energy involved in coalescence for situations on open surfaces and inside narrow gaps. For the sake of simplicity we firstly don't study the process dynamics but consider the potential energy before and after coalescence neglecting gravity, evaporation and the presence of the second liquid. In case of an open surface we assume that the drop shapes are equal to segments of ideal spheres. In case of the situation in the gap we assume that the droplets are in contact with both surfaces and that their shape is given by a cylinder out of which half a torus is cut. We find that the system energy is reduced by term ΔE consisting of a constant which includes the volume ratio of the droplets and the surface energies multiplied by the total volume to the power of 2/3 in case of an open system and multiplied by the total volume times the gap width to the power of 1/2 in case of confinement (**Fig. 4**). Due to the different exponents in contrast to intuition the driving forces in the gap are bigger, equal or smaller than on open surfaces.

2.5   Surfactants

Finally we discuss the impact of surfactants as intermediate layers. Surfactants make separation more difficult due to the reduction of the surface energies and thus the reduction of selectivity of wetting. But still under certain circumstances separation is conceivable: Hydrophilic droplets covered with a surfactant become hydrophobic hybrid objects and vice versa for hydrophobic droplets. The situation is analogous for hydrophilic and hydrophobic surfaces covered with surfactants. Thus the whole situation is inverted but with significantly reduced driving forces.

3   CONCLUSION

In conclusion we analyze the separation process of binary incompatible liquid mixtures (emulsions) on surfaces with an abrupt change of wettability using monodisperse Toluene- Water- emulsions. We identified fundamental process steps and developed a hydrodynamic model. Furthermore experimental and theoretical studies have been carried out to study droplet coalescence as a driving force of separation.

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