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Phoretic Phenomena of Colloidal Particles in a Dead-end Pore Microfluidic Channel

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Phoretic phenomena of colloidal particles in a dead-end pore microfluidic channel

by

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A THESIS

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Abstract

Colloidal particles can be manipulated under the gradient of an external field to transport them in the system toward desired locations. The motion of colloidal particles resulting from an imposed or self-generated concentration gradient is called diffusiophoresis which has been used in a wide range of applications such as drug delivery, wastewater treatment, and enhanced oil recovery. This phenomenon provides a low-cost and easy portable method to manipulate particles. Previous works investigated the diffusiophoretic motion of non-porous particles in microfluidic channels both experimentally and theoretically. However, the migration of porous particles under the effect of concentration gradient has not been studied experimentally. In this work, we have used a dead-end pore microfluidic channel to explore the diffusiophoretic motion of porous particles. For this purpose, we first study the migration of non-porous particles in the dead-end pore channel with and without the presence of background concentration gradients. Our results indicate a temporary self-generated concentration gradient is generated in the channel resulting from the interfacial interaction of PDMS walls with the ions present in DI water without introducing any background concentration gradient. In the presence of an electrolyte concentration gradient, the relative difference in the ions' diffusivity (β) and particles' zeta potential are two main effective factors on the diffusiophoretic motion of non-porous particles. In the next section, we study the diffusiophoretic motion of porous particles, and differences in the case of non-porous particles are investigated. In contrast to non-porous particles, porous particles' migration under the influence of concentration gradient is a function of pore size, surface area, and surface charge density. The surface charge density of porous particles can change significantly because of counterions diffusion into the porous particles which can result in inversion of motion direction. Therefore, the effect of the interior microstructure of colloidal particles is crucial in controlling their diffusiophoretic motion.

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Table Of Contents

Abstract.....	ii
Acknowledgments	iii
List Of Figures.....	vi
List of Tables	ix
Nomenclature	x
Chapter 1	1
Introduction.....	1
1.1 Motivation	2
1.2 Objectives.....	3
1.3 Tasks.....	3
1.4 Organization	4
Chapter 2	5
2 Background and Literature Review	5
2.1 Phoretic motion of colloidal particles	5
2.2 Microfluidics	7
2.3 Diffusiophoresis of colloidal particles in electrolyte solutions	9
2.3.1 Diffusiophoresis in a microfluidic device.....	11
2.3.2 Diffusiophoresis in a dead-end pore channel.....	12
2.3.3 PDMS interaction with the dissolved CO ₂ in a solution in the microfluidic channel 16	
2.4 Effect of the interior structure of colloids on their diffusiophoretic motion	17
Chapter 3	21
3 A self-generated exclusion zone in a dead-end pore microfluidic channel.....	21
3.1 Introduction	21
3.2 Experimental setup	23
3.2.1 PDMS Microfluidic Channel	23
3.2.2 Experimental Protocol.....	24
3.3 Results and discussion.....	24
3.3.1 Exclusion Zone in the dead-end pore geometry	24
3.3.2 Ion's boundary layer analysis	26
3.3.3 Particles' trajectory analysis.....	28

3.3.4	Evolution of the Exclusion zone.....	30
3.3.5	Balance between diffusiophoretic velocity and convective velocity	33
3.4	Conclusion.....	34
Chapter 4		36
4	The diffusiophoretic motion of porous and non-porous silica particles in a dead-end pore microfluidic channel	36
4.1	Introduction	36
4.2	Experimental setup	38
4.2.1	PDMS microfluidic channel.....	38
4.2.2	Salt solutions and particle suspension.....	40
4.2.3	Experimental protocol for microfluidic channel.....	40
4.2.4	Experimental protocol for drag force measurement	40
4.3	Results and discussion.....	41
4.3.1	Drag force measurement using optical tweezers.....	41
4.3.2	Diffusiophoretic motion of non-porous particles	43
4.3.3	Diffusiophoretic motion of porous particles	47
4.4	Conclusions	52
Chapter 5		55
5	Conclusions and Recommendations.....	55
5.1	Conclusions	55
5.2	Recommendations and Future Directions.....	58
Supplementary information for chapter 3.....		60
A 1.	Exclusion zone establishment over time.....	60
A 2.	Obtaining ions' exclusion zone thickness using boundary layer analysis.....	61
A 3.	Obtaining particles' exclusion zone thickness using particles' trajectory analysis...	64
A 4.	Exclusion zone development in the main channel for different flow rates	66
References		67

List Of Figures

Fig 2.1 Schematic representation of a charged particle under a concentration gradient in an electrolyte solution (NaCl). An electric field (E) is generated by the concentration gradient of NaCl, and a tangential pressure gradient in the electric double layer of the particle is produced due to the gradient of NaCl concentration. For the case of negative β like NaCl, both chemiphoresis and electrophoresis contribution drives the negatively charged particle towards higher ionic concentration. Reproduced from ref. 58 with permission from The Royal Society of Chemistry.	6
Fig 2.2 Schematic illustration of fabricating microfluidic channel using soft lithography technique. First, the degassed PDMS is poured on the silicon wafer. Second, after degassing the poured PDMS on the silicon wafer, the PDMS will be cured in the oven at 90 °C for 2 hours. Then, the cured PDMS can be peeled off and sealed to a glass slide. Reproduced from ref. 75 with permission from The Royal Society of Chemistry.	8
Fig 2.3 A schematic illustration of the experimental setup to visualize the phoretic motion of colloidal particles under a microscope. This figure includes two syringe pumps to inject the solution into a microchip, connecting tubes, a microchip, and a microscope to visualize the particles' motion. Adapted with permission from ref. 77. Copyright 2006 American Chemical Society.	9
Fig 2.4 Sketch of a set of dead-end pores in the microfluidic channel. The upper section is the main channel and the small branches are called dead-end pores. Adapted with permission from ref. 29. Copyright 2020 American Chemical Society.	12
Fig 2.5 Generating concentration gradient through the compaction experiment in a dead-pore channel. Initially, the pores are filled with the colloidal suspension (solution 1). Then an air plug following with the second solution is injected into the channel. The starting time of the experiment is after the two solutions come into contact at the entrance of the first pore. Adapted with permission from ref. 29. Copyright 2020 American Chemical Society.	13
Fig 2.6 Creating concentration gradient using entrainment approach in a dead-end pore microfluidic channel. First, the pores are filled with the electrolyte solution (solution 1), then, the colloidal suspension (solution 2) is flown into the channel after evacuating the main channel. Adapted with permission from ref. 29. Copyright 2020 American Chemical Society.	14
Fig 2.7 The trajectories of 1 μ m particles in a series of dead-end pores using the entrainment experiment approach with and without the presence of a concentration gradient. (a) In the absence of a concentration gradient in the pores, colloids will not be captured inside the pores and they just enter the entrance of the pores due to the hydrodynamic forces and flow geometry effect. (b) In the presence of an electrolyte concentration gradient (10mM of NaCl inside the pore and 0.1mM outside the pore), the particles migrate into the pores as a result of the diffusiophoretic velocity. The colloid tracks in the main channel are fainter than (a) due to the difference in the contrast settings during the image processing. Reproduced from ref. 67 with permission from The Royal Society of Chemistry.	15
Fig 2.8 Schematic illustration of the imposed velocities on the colloidal particle in the presence of a concentration gradient at the entrance of dead-end pores. The convective velocity originated from the ambient flow of the particle, the diffusiophoretic velocity is created due to the imposed	

concentration gradient in the pores, and the net velocity is the final velocity of the particle based on the balance between the diffusiophoretic velocity and convective velocity.....	16
Fig 2.9 The dimensionless diffusiophoretic velocity for charged porous particles as a function of dimensionless fixed charge density in the suspension with volume fraction 0.1 and $\lambda a = 1$ (highly permeable particles). (a) The dimensionless diffusiophoretic velocity when $\beta = 0$ means only chemiphoresis is contributing to trigger diffusiophoretic velocity. (b) The dimensionless diffusiophoretic velocity when $\beta = -0.2$ means both electrophoresis and chemiphoresis are contributing to the diffusiophoretic velocity. Adapted with permission from ref. 43. Copyright 2015 American Chemical Society.	19
Fig 3.1 Schematic configuration of the dead-end pore geometry and dimensions. After filling pores with DI water, a suspension of silica particles flows through the evacuated main channel and reaches a series of dead-end pores containing DI water.	23
Fig 3.2 A schematic representation (a) and experimental observation (b) of the exclusion zone formation in the main channel caused by a self-generated concentration gradient from the dead-end pores. (a) The blue dashed line represents the ionic exclusion zone, which is larger than the particle exclusion zone represented by the red line. A particle in the main channel experiences forces in the tangential direction as a result of the ion concentration gradient. Experimental observation of the exclusion layer formation in the dead-end channel for pore width = 100 μm	25
Fig 3.3 The experimental data of normalized particle exclusion thickness multiple by the square root of velocity for 2 μm silica particles. The orange square shows experimental data in $Q=80\mu\text{L/hr}$, and the black star is for 30 $\mu\text{L/hr}$. The pore width in this diagram is 100 μm	29
Fig 3.4 Comparing the exclusion zone thickness as a function of position over the first pore calculated in theory with experimental results for 2 μm silica particles. (a) For pore width=50 μm . (b) For pore width=100 μm . (c) For pore width=150 μm . The red curve represents the ionic exclusion thickness and the black curve displays the silica particles exclusion thickness.	29
Fig 3.5 Normalized exclusion zone thickness over time for 2 μm silica particles. (a) For pore width=50 μm . (b) For pore width=100 μm . (c) For pore width=150 μm	31
Fig 3.6 Normalized exclusion zone thickness over time for 1 μm silica particles. (a) For pore width=100 μm . (b) For pore width=150 μm	31
Fig 3.7 Effect of the particle size on the sustainability of the exclusion zone over time. This figure is plotted for the end-point ($y = 150\mu\text{m}$) of the first pore. The red curve and black curve represent 2 μm and 1 μm particles, respectively.	32
Fig 3.8 Effect of increasing flow rate on the maximum exclusion thickness based on the theoretical calculations and experimental observations for three different flow rates. The pore width in this diagram is 100 μm . Dashed lines show the ionic exclusion thickness and solid lines represent 2 μm silica particles exclusion thickness. (a) maximum exclusion thickness for each flow rate. (b) Scaling the dimensionless exclusion thickness by the inverse of the square root of the Sh number.	33

Fig 4.1 Schematic illustration of the dead-end pore geometry and dimensions. The pores are filled with solution 1 (electrolyte solution), then, solution 2 which is particle suspension in DI water is entered into the channel.	39
Fig 4.2 Drag force of 2 μm non-porous silica particles and porous silica particles as a function of velocity using the optical tweezers. Linear fits to represent Stokes' law are included (dashed lines). Also, the effect of the ratio of pore size to water molecule size is presented. The green line represents the non-porous drag force where the ratio of pore size to water molecule size is zero. The blue line represents 2 μm porous particles with 2 nm pores where the ratio of pore size to water molecule size is 7.4. The yellow line shows 2 μm porous particles with 100 nm pores where the ratio of pore size to water molecule size is 370.	42
Fig 4.3 Schematic illustration of negatively charged particles under the electrolyte concentration gradient. In this figure, the pore is filled with the electrolyte which the diffusivity of negative ions is higher than positive ions, and the particle suspension without any electrolyte is passing over the entrance of the pore. At the starting point ($t = 0$), the particles just reach the entrance of the pores. After reaching the entrance of the pore, they will migrate toward the inside of the pore under the influence of electrolyte concentration gradient. The mechanism happening at the entrance of the pore around the negatively charged particle is shown in the right hand side for the NaCl electrolyte as an example, where the slower effective motion of Na^+ results in an electric field that drives the negatively charged particles into the pore.	44
Fig 4.4 Entrainment of 1 μm non-porous silica particles into the pores in the presence of the electrolyte concentration gradient as a function of time. (a) Migrating of 1 μm non-porous silica particles under the NaCl concentration gradient. (b) The motion of 1 μm non-porous silica particles under the NaOH concentration gradient.	45
Fig 4.5 Dimensionless maximum position of 1 μm non-porous silica particles under the imposed electrolyte concentration gradient over time. The red squares and blue circles represent the influence of 10 mM NaOH and 10 mM NaCl, respectively.	46
Fig 4.6 Diffusiophoretic motion of porous silica particles under the concentration gradient of 10 mM NaCl. (a)Time sequence images for 1 μm porous silica particles with 2nm pores (b) Time sequence images for 1 μm porous silica particles with 10 nm pores.....	48
Fig 4.7 Scaled maximum position of 1 μm non-porous and porous silica particles under the 10 mM NaCl concentration gradient over time. The orange circles, green triangles, and red squares represent particles with pores of 2 nm, 10 nm, and non-porous particles respectively.	50
Fig 4.8 Diffusiophoretic motion of porous silica particles under the concentration gradient of 10mM NaOH. (a) Time sequence images for 1 μm porous silica particles with 2 nm pore size. (b) Time sequence images for 1 μm porous silica particles with 10 nm pore size.....	51

Fig. A1 Experimental observation of the exclusion zone formation in dead-end channel for pore width = 100 μm . (a) For 1 μm silica particles at $t=3\text{min}$ over the first pore. (b) For 2 μm silica particles at $t=3\text{min}$ over pores 4 to 6.....	60
Fig. A2 The ratio of normalized particle exclusion thickness in two flow rates. The black curve shows the experimental value in each position. The blue and red lines display the average values over the first pore in experiment and theory, respectively.....	65

List of Tables

Table 4.1 Zeta potential measurements of non-porous and porous particles with DLS instrument in DI water and 10 mM NaOH solution.....	52
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Nomenclature

U_{DP}	diffusiophoretic velocity
$C(\mathbf{x},t)$	solute concentration
D_{DP}	diffusiophoretic mobility of particles
κ^{-1}	Debye length
a	radius of the particle
β	relative diffusivity difference of anions and cations
ε	electrical permittivity of the solution
k_B	Boltzmann constant
T	absolute temperature
μ	viscosity of the solution,
z	valence of the ions
e	elementary charge
ζ_p	zeta potential of particles
E	electric field
w_{cs}	width of the cross-section
Re	Reynolds number
ρ	space charge density of mobile ions in the system
γ	friction coefficient representing the reduced drag force in a porous material,
p	fluid pressure
$\mathbf{v}$	fluid flow
ϕ	electric potential
λ^{-1}	Brinkman screening length
C_0	initial electrolyte concentration
$\bar{Q}$	dimensionless fixed-charge density,
A_1	mathematical function of permeability for the electrophoretic contribution

A_2	mathematical function of permeability for the chemiphoretic contribution
$\mathbf{n}$	outward normal vector
L_{ch}	channel length
Sh	Sherwood number

Chapter 1

Introduction

The phoretic motion of colloidal particles which is the transport of colloidal particles under the influence of external fields has been investigated for over fifty years[1]–[3] due to its wide range of applications in separation[4]–[8], wastewater treatment[9]–[11], drug delivery[12]–[20], enhanced oil recovery (EOR)[21]–[23], and many others. The typical external fields are a gradient in electrostatic potential, solute concentration, or temperature. The motion of colloidal particles under the effect of a solute concentration gradient is called diffusiophoresis[24]–[26]. The mechanism of this phenomenon in the presence of electrolytes or non-electrolytes is different. In most industrial applications, the presence of ions is common. The diffusiophoretic motion of colloidal particles in electrolytes has been widely studied both theoretically[27], [28] and experimentally[29]–[31]. Experimental studies have utilized microfluidic devices to analyze the diffusiophoretic motion of colloidal particles because microfluidics provides practical advantages such as a cost-effective process, carrying out experiments in a short time, high resolution, etc[32]. Among different materials for fabricating microfluidic channels, polydimethylsiloxane (PDMS) is the most popular[29], [30], [33]–[36]. PDMS has high gas permeability and negative surface charge which both can affect the motion of charged colloidal particles by introducing a temporary concentration gradient. However, the influence of these effects on the diffusiophoretic motion of colloidal particles has been relatively unexplored in literature.

Furthermore, the diffusiophoretic transport of non-porous particles has been explored in various studies both theoretically and experimentally; however, in reality, many colloidal particles are not non-porous but of porous nature meaning that they are permeable to the liquid medium and ions. Porous particles such as DNA, proteins, porous silica, etc are broadly used in various fields such as drug delivery and water treatment[37]. Therefore, it is important to understand their diffusiophoretic motion as diffusiophoresis is a potential technique to use in drug delivery and water treatment applications. The diffusiophoretic motion of charged porous particles has been investigated theoretically in limited studies in the last decade[38]–[41]; whereas, there is no experimental study on the migration of porous particles under the effect of a concentration gradient. Since various parameters such as pore size, porosity (defined as the volume of the pores

to the total volume), how the pores are connected, Debye length, and others can affect the migration of porous particles, further experimental and theoretical investigations are required to be able to predict their motion under the influence of concentration gradient.

1.1 Motivation

The work explained in this thesis is arising from a gap in the literature on two experimental aspects of diffusiophoresis. The first one is the motion of charged colloidal particles in a microfluidic channel under the influence of the surface chemistry of PDMS and the interaction of the PDMS wall with the fluid inside the channel. Second, the motion of porous particles under the effect of a concentration gradient in a microfluidic channel which has not been investigated experimentally. Therefore, we aim to study the effects of PDMS surface chemistry and the influence of its interaction with an aqueous fluid on the particles' phoretic motion. A better understanding of the effect of PDMS surface chemistry and the effects of this chemistry on particle motion will yield insights and understanding in many experimental microfluidic devices where charged colloidal particles suspended in a solution are moving through a microfluidic channel.

Additionally, we experimentally investigate the diffusiophoretic motion of porous particles in a microfluidic channel, which has been discussed in detail for non-porous particles in numerical and experimental studies. Theoretically, the migration of charged porous particles under an imposed concentration gradient depends on the surface charge, porosity, Debye length, volume fraction of particles in the solution, and difference in the ions' diffusion coefficient[38]. In theoretical studies, it has been proved as permeability increases, the diffusiophoretic velocity increases as well[41]. The permeability of porous particles which means passing fluid through the inside of particles can change by the way that pores are connected, pore size, and porosity of the interior of porous particles. Increasing the permeability reduces the imposed drag force on porous particles resulting in a higher velocity[42]. Therefore, various factors affect the permeability of porous particles which is not considered in the previous studies[38]–[41], [43]. Also, the surface charge of porous particles as another effective parameter on the diffusiophoretic velocity[39] is very important because it changes by entering counterions into the interior region of porous particles. Understanding the phoretic motion of porous particles under a concentration gradient can be applied in particle manipulating applications. This motivated us to explore the effect of porosity

as a function of pore size, and the effective surface charge of porous particles on their diffusiophoretic behavior under an electrolyte concentration gradient experimentally, which has relatively ample theoretical evidence.

1.2 Objectives

Based on the motivation for studying the motion of non-porous and porous colloidal particles in a microfluidic channel with and without the imposed concentration gradient, the following objectives are defined:

1. Investigate the influence of PDMS walls' interaction and surface chemistry with the aqueous fluid on the motion of colloidal particles in a microfluidic channel.
2. Measure the migration of charged porous particles with different porosity in the presence of an electrolyte concentration gradient using a microfluidic chip and compare their diffusiophoretic motion with that of non-porous particles.

1.3 Tasks

To answer the above-mentioned objectives the following steps are taken into account through this research:

1. The motion of non-porous particles will be visualized in a microfluidic channel to analyze the influence of PDMS interaction on the particles' migration in the channel along with considering the effect of flow velocity. Also, the effect of particle size on their motion will be observed and analyzed.
2. The difference in hydrodynamic forces between porous and non-porous particles will be measured using an optical tweezers instrument.
3. The diffusiophoretic motion of porous particles with different porosity in a microfluidic channel will be investigated and their motion under the concentration gradient of two different electrolytes with different ions diffusivity will be compared with non-porous particles.

1.4 Organization

This thesis is organized in the following manner: Chapter 2 provides a background and literature review on the diffusiophoretic motion of colloidal particles in microfluidic channels. Chapter 3 covers the details of the motion of colloidal particles in a microfluidic channel and the effect of PDMS wall interaction on particles' migration. Chapter 4 discusses the motion of porous and non-porous particles under the electrolyte concentration gradient in a microfluidic channel. Also, the drag force comparison of porous particles with non-porous particles measured by an optical tweezer is covered in this chapter. Chapter 5 provides a summary of the results and conclusion of the work done as well as recommendations for future studies on our topic.

Chapter 2

2 Background and Literature Review

This chapter focuses on providing a brief literature review of investigations that have been done on the phoretic motion of colloidal particles under a concentration gradient, and the experimental studies of this phenomenon in a microfluidic channel. This chapter starts with an introduction to phoretic motion in general. Then, we provide an overview of microfluidics as the experimental work of this thesis has been done in a microfluidic channel. Afterwards, the phoretic motion of colloidal particles under a concentration gradient (diffusiophoresis) is explained in more detail in a solution, and in a specific microfluidic geometry that is relevant to our work. In the final section, the influence of the colloids' interior structure on their diffusiophoretic motion is elaborated. Also, the gaps related to this topic will be identified.

2.1 Phoretic motion of colloidal particles

The migration of colloidal particles under imposed external fields is termed phoretic motion. The external field that leads to the transport of particles can originate from a gradient in solute concentration (diffusiophoresis), electrostatic potential (electrophoresis), or temperature (thermophoresis). The motion of particles under these gradients is produced by the interaction of the ambient fluid with the interfacial structure near the particles' surfaces[44]–[46]. Phoretic motion has two important characteristics: first, the origin of this motion is within the interfacial diffuse layer near the particle's surface which is the electric double layer for charged particles, and other surface interactions characterized by a diffuse interface of finite thickness. The fluid is displaced relative to the particles within the diffuse layer due to the osmotic pressure[47], [48]. Second, the motion of the particle is force-free and the particle moves at a steady velocity[49]. In this thesis, we focused on the migration of colloidal particles under a concentration gradient of solute molecules.

The motion of colloidal particles resulting from an imposed or self-generated concentration gradient is called diffusiophoresis and has been widely used in various fields such as drug delivery,

wastewater treatment, separation, laundry detergency, and enhanced oil recovery [50]–[56]. In general, there are two types of diffusiophoresis in the presence of or without electrolytes. In electrolytes, the concentration gradient of solute molecules causes particle transport by the generation of a local electric field (electrophoresis) and pressure field in the Debye layer (chemiphoresis). Therefore, a combined influence of electrophoresis and chemiphoresis drives particles under gradients of electrolyte solution. The electrophoresis contribution leads to the particle motion due to the induced electric field as a result of a difference in the cations' and anions' diffusivities. Simultaneously, the chemiphoresis contribution produces the osmotic pressure gradient along a particle surface in the presence of local solute gradients which drives particles in the solution as shown in Fig 2.1[57], [58].

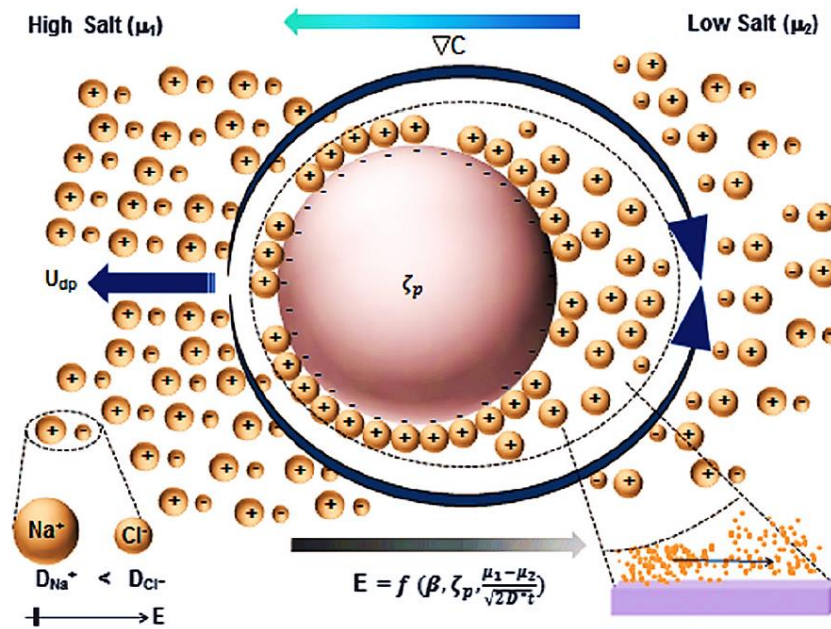


Fig 2.1 Schematic representation of a charged particle under a concentration gradient in an electrolyte solution (NaCl). An electric field (E) is generated by the concentration gradient of NaCl, and a tangential pressure gradient in the electric double layer of the particle is produced due to the gradient of NaCl concentration. For the case of negative β like NaCl, both chemiphoresis and electrophoresis contribution drives the negatively charged particle towards higher ionic concentration. Reproduced from ref. 58 with permission from The Royal Society of Chemistry.

The osmotic pressure gradient along the particle surface generates a fluid flow along the particle surface which is called diffusioosmosis. In non-electrolytes, the transport of particles is solely

through the contribution of chemiphoresis due to particle-solute interactions such as van der Waals interactions or steric exclusion[44], [57], [58].

2.2 Microfluidics

Microfluidics is a field of study of fabricating, designing, and utilizing of systems that deal with the transport and manipulation of small amounts of fluids (10^{-9} to 10^{-18} liters) in small channels with characteristic dimensions of tens to hundreds of micrometers. This technology offers new useful capabilities compared to large-scale protocols such as less sample or reagent consumption, detecting and controlling the experiment with high resolution and sensitivity, low-cost process, running experiments in a short time, reduced risk of contamination, laminar flow, and ability to carry out multiple processes in parallel[32], [59], [60]. In recent years, microfluidics has been widely used to manipulate the phoretic motion of particles under a gradient of electric potential[61]–[63], temperature[64]–[66], and concentration[29], [30], [52], [57], [67]–[69] as the particles' motion can be visualized with a high resolution.

The current common prototyping of microchannels involves fabricating patterns of the microfluidic channel on a substrate. A popular prototyping process is utilizing soft lithography procedures[70]. For using this method, a design of the channel is created in software such as CAD or KLayout which is printed on a photo mask. Then, the pattern will be printed on a master mold which is the silicon wafer. Afterwards, the master mold (silicon wafer) is silanized using trichlorosilane (HSiCl_3) to create a hydrophobic surface on the master mold to easily separate the PDMS from the silicon wafer. PDMS is prepared by mixing PDMS monomer with a curing agent in a ratio of 10:1 by weight. The degassed mixture of PDMS is poured into the master mold. Afterward, the master mold filled with PDMS mixture is degassed in a vacuum desiccator to remove air bubbles inside the mixture. Finally, the cured PDMS can be peeled from the master mold and sealed to a neat glass slide via a plasma bonding process[60], [71]–[75]. The schematic illustration is shown in Fig 2.2[75]. Generating microfluidic devices via soft lithography has several advantages such as a cost-efficient process, easy to replicate, and generation of multiple microfluidic devices of the same master mold in a short time[72], [76].

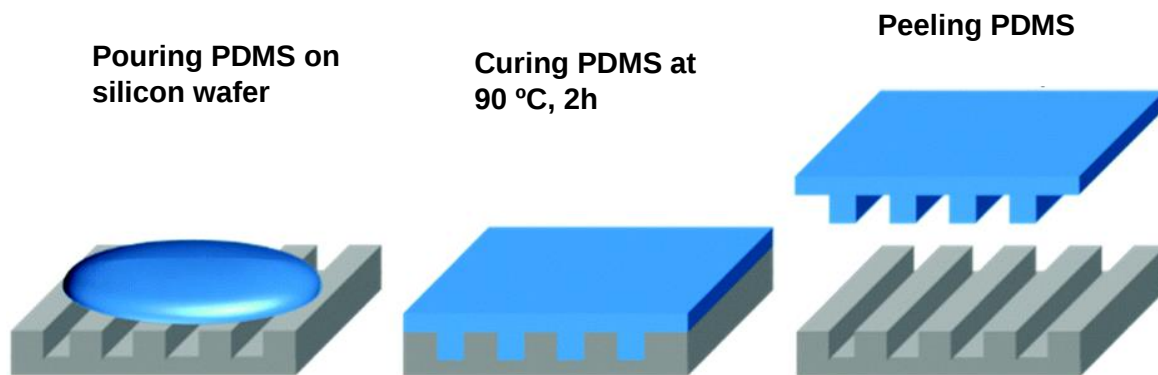


Fig 2.2 Schematic illustration of fabricating microfluidic channel using soft lithography technique. First, the degassed PDMS is poured on the silicon wafer. Second, after degassing the poured PDMS on the silicon wafer, the PDMS will be cured in the oven at 90 °C for 2 hours. Then, the cured PDMS can be peeled off and sealed to a glass slide. Reproduced from ref. 75 with permission from The Royal Society of Chemistry.

PDMS microfluidic channels provide the opportunity to obtain comprehensive information on the phoretic motion of particles under the effect of a gradient in electric potential, temperature, or solute concentration. The transparent nature of PDMS and the laminar flow in the microchannels are of great help to visualize the phoretic motion of colloidal particles and analyze their migration[59]. A schematic representation of the experimental setup to observe the phoretic motion of particles is shown in Fig 2.3 which shows the syringe pumps, connecting tubes, microscope, and microchannel[77]. Based on the field gradient, the setup can be modified to create the desired gradient in the channel.

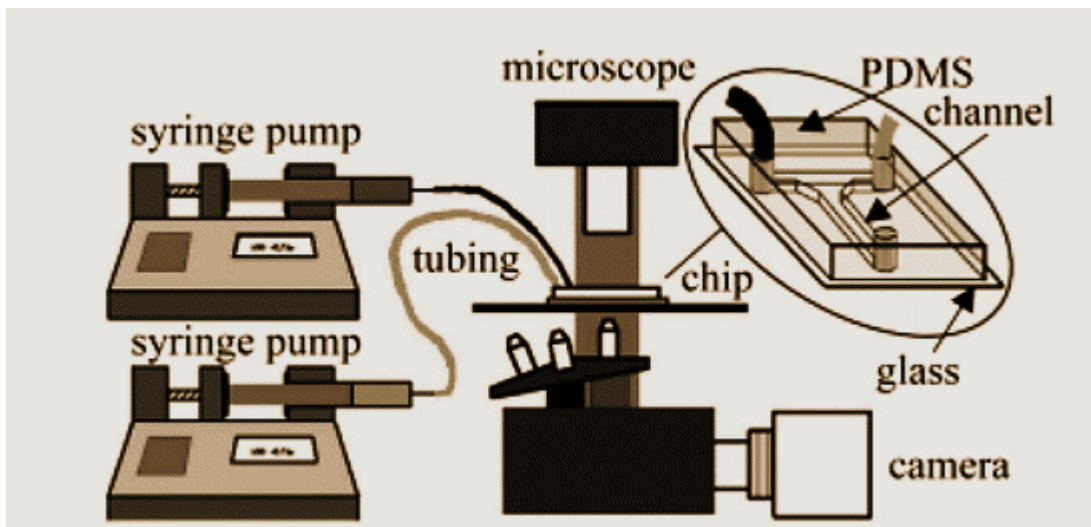


Fig 2.3 A schematic illustration of the experimental setup to visualize the phoretic motion of colloidal particles under a microscope. This figure includes two syringe pumps to inject the solution into a microchip, connecting tubes, a microchip, and a microscope to visualize the particles' motion. Adapted with permission from ref. 77. Copyright 2006 American Chemical Society.

2.3 Diffusiophoresis of colloidal particles in electrolyte solutions

The concept of diffusiophoresis was first introduced in the 1940s by Derjaguin et al. for nonelectrolytes in the form of capillary osmosis. Further investigations have been discussed for electrolyte solutions by Anderson and Prieve in the 1980s[44]–[46]. In reality, the presence of ions plays an important role in various applications. Therefore, we focus on the behavior of charged particles in electrolyte solutions under the concentration gradient of solute molecules or ions. Fig 2.1 shows a schematic illustration of charged particles within the concentration gradient of NaCl electrolyte[58]. For electrolyte solutions, concentration gradients of cations and anions with different diffusivities create a local electric field, in which the charged particle will experience electrophoretic motion. In the case of a thin Debye layer (Debye length (κ^{-1}) $\ll$ radius of the particle (a)) and symmetric electrolyte ($z:z$), the electrophoretic contribution is proportional to the diffusivity difference factor $\beta = (D_+ - D_-)/(D_+ + D_-)$ where D_+ is the diffusivity of cations and D_- is the diffusivity of anions in the solution[29], [30]. Additionally, a local gradient in the osmotic pressure near the surface of particles, resulting from locally different solute concentrations, causes the chemiphoretic migration of colloidal particles.

The contribution of both the electrophoresis and chemiphoresis components affects the overall diffusiophoretic velocity ($\mathbf{U}_{DP}$) of charged non-porous particles in a symmetric electrolyte (shown in Fig 2.1) which is defined as[58]

$$\mathbf{U}_{DP} = D_{DP} \nabla \ln C \quad (2.1)$$

Here $C(\mathbf{x},t)$ is the solute concentration as a function of position and time and D_{DP} is the diffusiophoretic mobility of particles. The diffusiophoretic mobility in the thin double-layer approximation ($\kappa^{-1} \ll a$) and symmetric electrolytes is defined as[67]

$$D_{DP} = \frac{\varepsilon k_B T}{\mu z e} \left[\beta \zeta_p + \frac{4 k_B T}{z e} \ln \left(\cosh \left(\frac{z e \zeta_p}{4 k_B T} \right) \right) \right] \quad (2.2)$$

Where ε is the electrical permittivity of the solution, k_B is the Boltzmann constant, T is the absolute temperature, μ is the viscosity of the solution, z is the valence of the ions, e is the elementary charge, and ζ_p is the zeta potential of particles[67]. The zeta potential is the electric potential at the location of the slipping plane in the interfacial electric double layer[78]. The first term in eq (2.2) originates from the electrophoretic effect, and the second term accounts for the chemiphoresis contribution[79].

Also, the generated electric field due to the presence of ionic concentration gradient can be quantitatively calculated as[58], [80]

$$\mathbf{E} = \frac{kT}{ze} \beta \frac{\nabla C}{C} \quad (2.3)$$

Thus, the key components causing diffusiophoretic transport of particles are 1) the presence of a concentration gradient of solute molecule in the solution, 2) the zeta potential of the particle, and 3) a difference in diffusivities of cations and anions.

As shown in Fig 2.1, for the NaCl electrolyte solution, β is negative because the diffusivity of anions (Cl^-) is larger than cations (Na^+). In this case, a negatively charged particle tends to move toward the higher ionic concentration as a result of the electrophoretic contribution. Also, the tangential pressure gradient along the particle's surface drives the particle toward a higher concentration of ions due to the van der Waals attraction forces. Therefore, both the electrophoretic

and chemiphoretic contributions lead to the negatively charged particle's transport in the same direction in the NaCl solution[58], [81].

On the other hand, when the diffusivity of cations is higher than anions in the solution, the negatively charged particle moves toward lower ionic concentration based on the electrophoretic velocity, and the chemiphoretic velocity drives the particle toward higher concentration if there is an attractive interaction between the solute molecule and the particle. In this case, the electrophoresis and chemiophoresis will act in the opposite direction which creates a lower diffusiophoretic velocity compared to the previous case[81], [82].

For positively charged particles, the electrophoretic contribution would be different from negative particles. When the diffusivity of cations is higher than anions, the positively charged particles tend to move toward higher electrolyte concentration; whereas, positively charged particles migrate toward lower electrolyte concentration when the diffusivity of anions is larger than cations[58].

Typically, under the electrolyte concentration gradient, the particles' motion direction contributed by electrophoresis is determined by the sign of the particle's surface charge (ζ_p) and the relative difference in the ionic diffusivity (β). If $\beta\zeta_p > 0$, particles migrate toward the higher electrolyte concentration, and if $\beta\zeta_p < 0$, particles transport along the lower electrolyte concentration[39].

2.3.1 Diffusiophoresis in a microfluidic device

Verifying the enhancement of particle mobility via using microfluidics was studied in 2008 by Abécassis et al. after 60 years of development in theoretical descriptions of diffusiophoresis [69], [83]. The main physical concepts and theoretical models of diffusiophoresis can be confirmed using microfluidic channels in experiments[84]. Along with the improvement of microfluidics, more experimental studies of diffusiophoresis were reported for various channel configurations such as dead-end pores, Hele-Shaw cells, and reacting walls[29]–[31], [34], [35], [55], [67], [85]–[89].

The fundamental role of microfluidic experiments is the ability to generate the desired concentration gradient of solute molecules which leads to the corresponding particle motion. In microfluidic channels, often the observed particle migration is not solely affected by

diffusiophoresis due to the charged surfaces of the system (e.g. PDMS channel walls) and the existence of bulk fluid flow. Setting up an ionic concentration gradient naturally produces diffusioosmosis along the channel wall due to the charged surface of typical wall materials like glass, PDMS, or PMMA (poly(methyl methacrylate))[69], [78], [81], [90]. These materials have similar surface charges with commonly used particles like polystyrene, silica, etc., which means that the order of magnitude of the diffusioosmotic velocity along the channel wall and the particles' diffusiophoretic velocity are comparable. The influence of diffusioosmosis is one of the crucial complications in microfluidic analyses for calculating the experimental diffusiophoretic velocity. Therefore, the effect of the diffusioosmotic slip velocity should be considered in calculating the net diffusiophoretic velocity in the microfluidic channel[30], [67].

2.3.2 Diffusiophoresis in a dead-end pore channel

Manipulation of colloids in dead-end geometries is commonly used in various applications such as drug delivery and underground oil and gas recovery. In this kind of geometry, Brownian motion is the sole natural mechanism that enables the transport of colloids into or out of pores, but this mechanism is extremely slow and inefficient for microscale particle migration. Thus, there is a scope for increasing the transport of colloids into or out of the pore through introducing a solute gradient. Depending on the ions' diffusivity, the migration of colloidal particles into the dead-end pore can be either enhanced or prevented[55], [85].

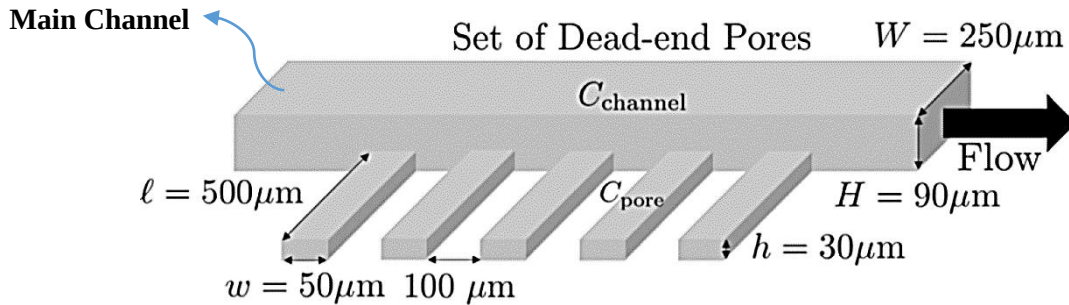


Fig 2.4 Sketch of a set of dead-end pores in the microfluidic channel. The upper section is the main channel and the small branches are called dead-end pores. Adapted with permission from ref. 29. Copyright 2020 American Chemical Society.

A dead-end pore geometry allows for generating a one-dimensional concentration gradient of solutes to analyze and visualize the diffusiophoretic motion of colloids. A schematic representation of a series of dead-end pores in a microfluidic device is shown in Fig 2.4[29]. The upper side in this figure is the main channel where the fluid flows in it via connecting a syringe pump to the entrance of the channel. The branches of the channel are dead-end pores where the solute concentration gradient is established along the length of the pores.

In contradiction to electrophoresis or thermophoresis where the gradient field is typically constant, the produced concentration gradients in this configuration are time-dependent. To generate a concentration gradient of solute in this channel, the entrance of the main channel is connected to a syringe pump that contains solution 1. Once solution 1 has filled the main channel, blocking the outlet of the channel drives the solution into the pores. After filling the whole channel with solution 1, the plug blocking the outlet is removed and the main channel is evacuated using an air plug. Once the main channel is empty, solution 2 will be injected into the channel. To prevent the mixing of two solutions, an air plug is introduced into the main channel before injecting solution 2[29], [30], [67].

Typically, two different approaches have been followed in this geometry to create the solute concentration gradient and visualize the particles' migration. The first approach is a compaction experiment where the pores are initially filled with solution 1 which is the colloidal suspension. Then, solution 2 which is the solution without particles is entered into the channel to produce the concentration gradient as shown in Fig 2.5[29].

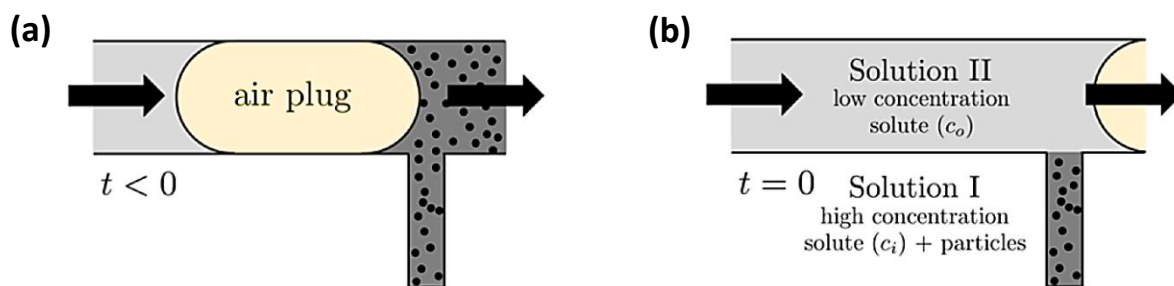


Fig 2.5 Generating concentration gradient through the compaction experiment in a dead-pore channel. Initially, the pores are filled with the colloidal suspension (solution 1). Then an air plug following with the second solution is injected into the channel. The starting time of the experiment is after the two solutions come into contact at the entrance of the first pore. Adapted with permission from ref. 29. Copyright 2020 American Chemical Society.

The second technique for creating a concentration gradient in dead-end pores channels is an entrainment experiment where the pores are filled with solution 1 which is the electrolyte solution without colloids. Afterward, the colloidal suspension (solution 2) is injected into the channel after evacuating the main channel with the air bubble which is shown in Fig 2.6.

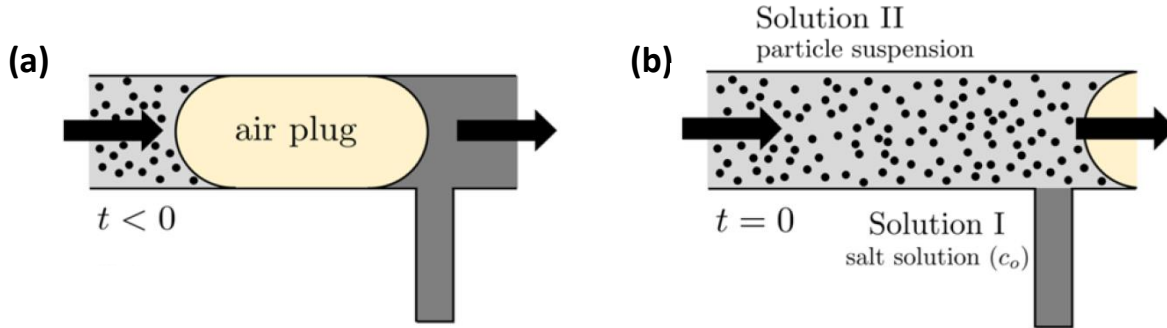


Fig 2.6 Creating concentration gradient using entrainment approach in a dead-end pore microfluidic channel. First, the pores are filled with the electrolyte solution (solution 1), then, the colloidal suspension (solution 2) is flown into the channel after evacuating the main channel. Adapted with permission from ref. 29. Copyright 2020 American Chemical Society.

The critical issue in the compaction experiment is the concentration of the electrolyte in the colloidal suspension because the particles stuck to the channel walls or aggregate when suspended in the solution with a high concentration of electrolyte (such as 10mM). For this study, we select the entrainment experiment to analyze and observe the diffusiophoretic motion of colloids to avoid the aggregation and sticking of colloids to the channel walls problems.

Furthermore, various studies verify that particle capture and migration along the pore length will not happen in the absence of a concentration gradient in the pores. As shown in Fig 2.7(a), the particles can penetrate the entrance of the pore via hydrodynamic forces and the presence of vortices but they cannot diffuse more along the length of the pores and ultimately escape[67]. The penetration length of particles at the entrance of the pores due to the hydrodynamic forces is called entrance length. There are various equations to calculate the entrance length depending on the channel geometry and the range of Reynolds numbers[91]–[95]. For rectangular geometry which is common geometry used for the diffusiophoresis phenomenon, the entrance length can be calculated as[94]

$$L_e = (w_{cs}) * \left(\frac{0.55}{1 + 0.13Re} + 0.065Re \right) \quad (2.4)$$

L_e is the entrance length, w_{cs} is the width of the cross-section and Re is the Reynolds number which is defined as $Re = \rho u w_{cs} / \mu$ for a rectangular channel in which w_{cs} is the larger side.

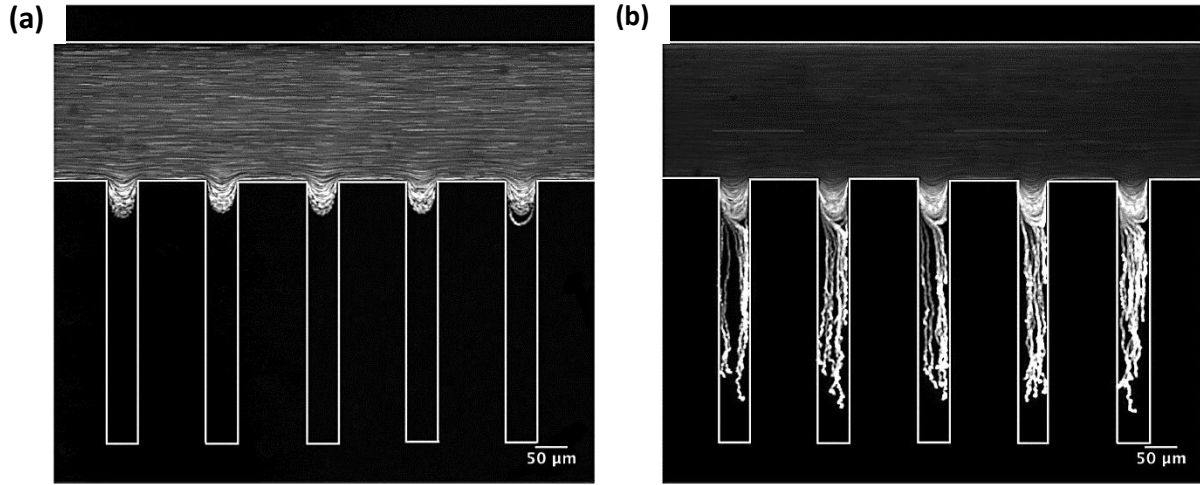


Fig 2.7 The trajectories of $1\mu\text{m}$ particles in a series of dead-end pores using the entrainment experiment approach with and without the presence of a concentration gradient. (a) In the absence of a concentration gradient in the pores, colloids will not be captured inside the pores and they just enter the entrance of the pores due to the hydrodynamic forces and flow geometry effect. (b) In the presence of an electrolyte concentration gradient (10mM of NaCl inside the pore and 0.1mM outside the pore), the particles migrate into the pores as a result of the diffusiophoretic velocity. The colloid tracks in the main channel are fainter than (a) due to the difference in the contrast settings during the image processing. Reproduced from ref. 67 with permission from The Royal Society of Chemistry.

On the other hand, the particles diffuse inside the pores in the presence of a concentration gradient shown in Fig 2.7(b)[67]. In the presence of a concentration gradient in dead-end pores, the velocity of colloidal particles at the entrance of the pores is a balance between the convective velocity ($\mathbf{U}_{\text{conv}}$) and the diffusiophoretic velocity ($\mathbf{U}_{DP}$) as displayed in Fig 2.8[51]. Therefore, the convective velocity, which is controlled by the pump flow rate, plays an important role in the dead-end pore geometry. As the flow rate changes, the balance between the diffusiophoretic velocity and the convective velocity changes as well. For instance, increasing the flow rate will increase the influence of the convective velocity on the net velocity and make it to be more dominant which means the possibility of particles' capturing inside the pores will diminish.

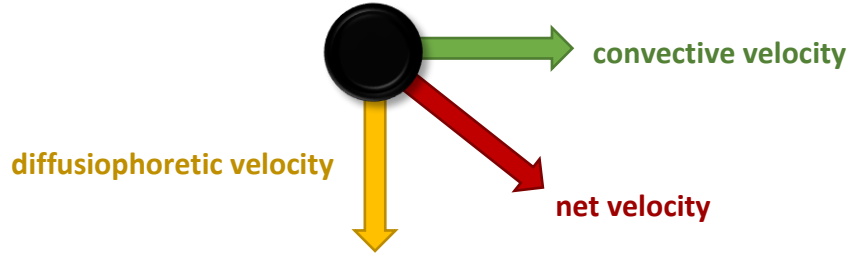


Fig 2.8 Schematic illustration of the imposed velocities on the colloidal particle in the presence of a concentration gradient at the entrance of dead-end pores. The convective velocity originated from the ambient flow of the particle, the diffusiophoretic velocity is created due to the imposed concentration gradient in the pores, and the net velocity is the final velocity of the particle based on the balance between the diffusiophoretic velocity and convective velocity.

2.3.3 PDMS interaction with the dissolved CO₂ in a solution in the microfluidic channel

When a suspension of colloidal particles flows in a microfluidic channel at a constant flow rate, a uniform dispersion of particles in the channel is expected. However, an unexpected accumulation of colloidal particles can take place in the channel without imposing any gradient inside the microfluidic channel[96]. The spontaneous transport of particles can happen due to gas leakage through permeable walls and the interaction of the PDMS wall with a solution. PDMS is the most popular material to fabricate microfluidic channels which has a high gas permeability and a negative surface charge[96]. The dissolution of the atmospheric CO₂ in the aqueous solution and the interaction of the pre-dissolved CO₂ with the PDMS wall can have a large impact on the micro-scale transports[97]. Dissolution of CO₂ in an aqueous solution ($\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$, $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$) generates H⁺, HCO₃⁻, and CO₃²⁻ ions. This dissolution of gas can create a self-generated ions concentration gradient in the flow which can drive particles in a specific direction due to the diffusiophoresis phenomenon[96]. Also, the importance of this small amount of concentration gradient stems from the large difference in the H⁺ diffusivity ($D_{\text{H}^+} = 9.3 \times 10^{-9} \text{m}^2 \text{s}^{-1}$) and HCO₃⁻ diffusivity ($D_{\text{HCO}_3^-} = 1.2 \times 10^{-9} \text{m}^2 \text{s}^{-1}$). This large difference creates a large electric field based on eq (2.3) resulting in the transport of colloidal particles in the channel.

Therefore, a self-generated concentration gradient of solute can form in a microfluidic channel and create a diffusiophoretic motion of charged colloids. This spontaneous phenomenon can suggest various potential applications such as particle collecting and concentrating. In the first part of our

work, we investigate the influence of the dissolved CO₂ in DI water and its interaction with the PDMS walls in a dead-end pore geometry on the particles' motion.

2.4 Effect of the interior structure of colloids on their diffusiophoretic motion

The diffusiophoretic motion of non-porous particles has been widely explored in various theoretical and experimental studies[27]–[30], [57], [98]–[101]. However, many colloidal particles have a porous structure and they are permeable to the liquid medium such as proteins, DNAs, porous silica, etc[102]–[104]. Thus, understanding the diffusiophoretic motion of porous particles both theoretically and experimentally is very important for applications in drug delivery, wastewater, and separation fields where using porous particles is relevant[105]. There are two crucial differences between non-porous particles and porous particles which distinguish their diffusiophoretic motion. The first difference is the overall hydrodynamic drag force for porous particles is much smaller than for hard particles due to the permeability of fluid through the interior region of porous particles[38]. The second difference arises from the distribution of charges over the entire interior of porous particles; however, the surface charges of hard particles are distributed only on the particle surface. In the case of the thin double layer ($\kappa^{-1} \ll a$), the influence of the reduced hydrodynamic drag force and distribution of surface charges all over the interior region of porous particles can cause orders of magnitude larger mobility compared to hard particles[37], [38], [105]–[107].

Moreover, the fixed charges carried by the porous particle can be neutralized by driving counterions into the interior region of porous particles when the Debye length layer is thin (large value of κa). This phenomenon is called “counterion condensation” or “shielding effect” which can reduce the chemiphoretic contribution to the phoretic motion of porous particles[38], [105], and even can neutralize the effect of chemiphoresis on the particle's mobility because the porous particle at very large κa is essentially chargeless.

The diffusiophoretic motion of porous particles has been investigated in a few theoretical studies in different aspects but there is a gap in the experimental analysis of the motion of the porous particles under the concentration gradient[38]–[41], [43], [69]. Thus, we experimentally investigate the difference in porous and hard particles' migration in the presence of a solute concentration gradient.

Eq (2.1) & (2.2) are derived for calculating the diffusiophoretic velocity of hard sphere particles. To drive the diffusiophoretic velocity for porous particles, the modified Stokes equation for Newtonian fluid with an extra term accounting for the local electric body force should be considered as follows [43]

$$-\nabla p + \mu \nabla^2 \mathbf{v} - \rho \nabla \phi - \gamma \mathbf{v} = 0, \quad 0 < r < a \quad (2.5)$$

$$-\nabla p + \mu \nabla^2 \mathbf{v} - \rho \nabla \phi = 0, \quad a < r < \infty \quad (2.6)$$

ρ is the space charge density of mobile ions in the system, γ is the friction coefficient representing the reduced drag force in a porous material, p is the fluid pressure, $\mathbf{v}$ is the fluid flow, and ϕ is the electric potential. The permeability of the porous particles can be characterized by using the Brinkman screening length (λ^{-1}). The Brinkman screening length is calculated through $\lambda^{-1} = (\gamma/\mu)^{0.5}$, and λa is its dimensionless form. As the λa becomes smaller, the particle permeability of the fluid is increased[41], [43]. The first term ($-\nabla p$) in eq (2.5) states the pressure gradient which prevents motion due to normal stresses. The second term ($\mu \nabla^2 \mathbf{v}$) represents the internal stress forces or viscous effects. The third term and fourth terms show the local electric body force and the reduced drag force inside porous particles, respectively[108].

Considering the modified Stokes equation, Gauss theorem, the conservation of ions, and the incompressibility constraint of the fluid flow resulting in the following diffusiophoretic velocity for porous particles[43]

$$\mathbf{U}_{DP} = \frac{\varepsilon}{\mu} \frac{|\nabla C|}{C_0} \left(\frac{kT}{ze} \right)^2 [(\kappa a)^2 \beta A_1 \bar{Q} + (\kappa a)^4 A_2 \bar{Q}^2] + O(\bar{Q}^3) \quad (2.7)$$

C_0 is the initial electrolyte concentration, a is the radius of the colloidal particle, $\bar{Q} = \frac{ZeQ}{\varepsilon \kappa^2 kT}$ is a dimensionless fixed-charge density, A_1 and A_2 are functions of permeability, the volume fraction of particles, and the electrokinetic radius (κa). A_1 represents the electrophoretic contribution in the diffusiophoretic velocity, and A_2 shows the contribution of chemiphoresis.

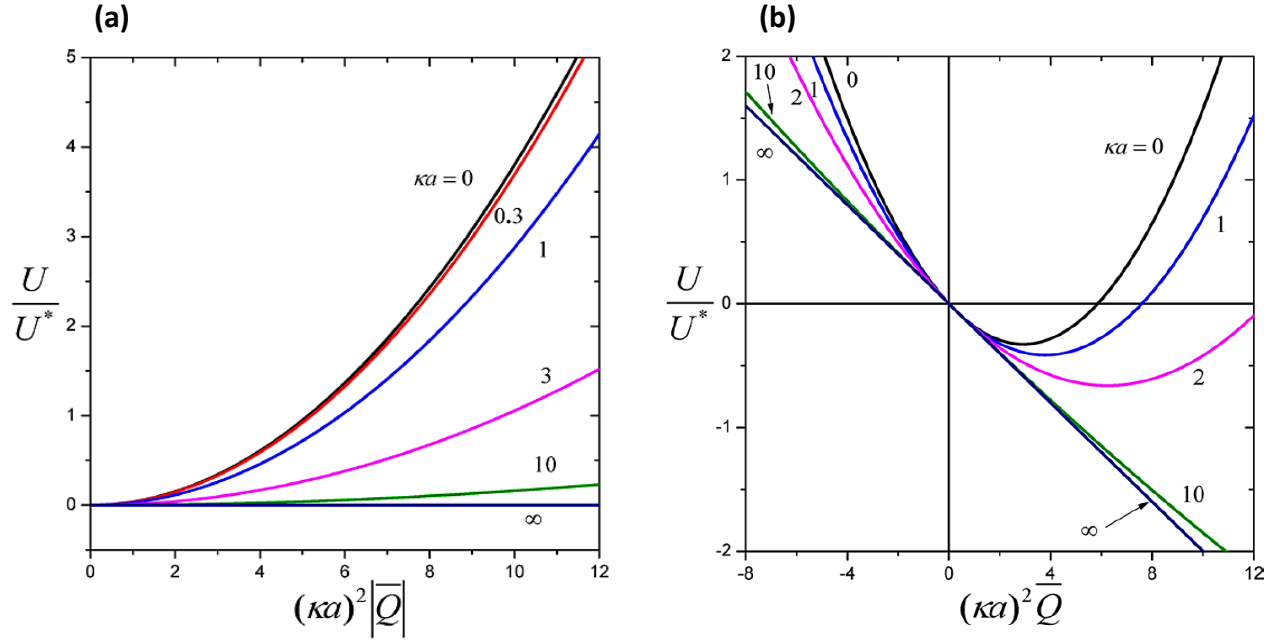


Fig 2.9 The dimensionless diffusiophoretic velocity for charged porous particles as a function of dimensionless fixed charge density in the suspension with volume fraction 0.1 and $\lambda a = 1$ (highly permeable particles). (a) The dimensionless diffusiophoretic velocity when $\beta = 0$ means only chemiophoresis is contributing to trigger diffusiophoretic velocity. (b) The dimensionless diffusiophoretic velocity when $\beta = -0.2$ means both electrophoresis and chemiophoresis are contributing to the diffusiophoretic velocity. Adapted with permission from ref. 43. Copyright 2015 American Chemical Society.

The variation of A_1 and A_2 functions have been studied by Huang et al.[43] for different ranges of permeability, volume fraction, and Debye length layer. They have shown that the diffusiophoretic mobility in a suspension of porous particles is a complex function of the permeability of the colloidal particle, volume fraction, surface charge of particles, the relative difference in the anions and cations diffusivities (β), and Debye length in the solution. Also, Lee's theoretical study[38] verifies the complex dependency of porous particles' diffusiophoretic velocity on the mentioned parameters; whereas, the diffusiophoretic mobility of hard spheres (eq (2.2)) depends on the zeta potential of particles and the relative difference in the ions' diffusivity.

Furthermore, two important ranges of κa can completely change the behavior of porous particles under a concentration gradient. For finite κa (less than 1) which means the size of the Debye layer is comparable with the particle's radius, the double-layer polarization effect becomes important,

and for large κa , the counterion condensation effect should be considered. As shown in Fig 2.9(a), the diffusiophoretic velocity of charged porous particles with increasing κa decreases. For large κa , it shows the diffusiophoretic velocity which is due to the counterion condensation effect. Also, the diffusiophoretic velocity of porous particles as a function of dimensionless fixed charged density in different κa in the presence of both chemiphoretic and electrophoretic contributions is shown in Fig 2.9(b). The diffusiophoretic velocity in this picture is more complicated than part (a) where just chemiphoretic contribution is available. As shown in Fig 2.9(b), the diffusiophoretic velocity increases as κa increases but for the small κa , the behavior is not monotonic due to the double-layer polarization effect. Moreover, in the range of low dimensionless fixed charge density ($(\kappa a)^2 \bar{Q} < 1$), the dimensionless diffusiophoretic velocity is very small and close to zero for all values of κa . Therefore, both the dimensionless fixed charge density and κa values are critical parameters in calculating the diffusiophoretic velocity.

In our work, we experimentally studied the effect of the porosity of particles on their diffusiophoretic motion in a microfluidic channel for the case of large κa and compared the results for porous particles with hard particles under a similar electrolyte concentration gradient.

Therefore, two topics in the diffusiophoretic in a dead-end pore microfluidic channel will be investigated in this thesis. The first one is to study the effect of dissolved CO_2 and the impact of PDMS surface chemistry in altering its equilibrium dissociation in DI water on the particles' motion in the dead-end pore microfluidic channel without introducing any concentration gradient to the channel. The second one is to explore the diffusiophoretic motion for porous particles as a function of pore size (which changes the porosity as well) and compare it to non-porous particles under the same conditions.

Chapter 3

3 A self-generated exclusion zone in a dead-end pore microfluidic channel

The work presented in this chapter is currently under review for publication as a research article in Lab On a Chip Journal.

3.1 Introduction

One of the most striking self-driven phenomena is the natural migration of colloidal particles under a self-generated or imposed concentration gradient, called diffusiophoresis. This migration of colloidal particles finds applications in water filtration[68], [109]–[111], microfluidic microdialysis[112], antifouling coatings[54], [89], [113], actuators and self-propelled motors[114], [115]. The repulsion of colloidal particles in an aqueous solution from an interface over distances of up to hundreds of micrometers results in a particle-free zone in the vicinity of the surface even if there are no external driving forces present. This so-called exclusion zone phenomenon has been observed near a wide range of materials, including biological tissues, hydrogels, hydrophilic polymers, and metals [116]–[119]. One of the intriguing characteristics of the exclusion zone is the remarkably long particle-repelling range which extends far beyond the Debye length [88], [89], [120]. Generally, the thickness of the exclusion zone varies from several tens to several hundreds of micrometers depending on the suspended colloidal particles, properties of the surface, the medium, and pH [116], [121]. While various explanations and mechanisms have been proposed for the exclusion zone formation, the exact physical origin has remained ambiguous [119], [122]–[125]. However, recent studies have suggested that a combination of a pH gradient near the surface, ion-exchange at the surface, diffusion of ions, and diffusiophoresis of suspended particles in the resulting ions' concentration gradient are playing key roles in the formation of the exclusion zone [31], [88], [110], [119], [123]. The concentration gradient of ions causes the migration of colloidal particles because of electrophoresis and chemiophoresis. The concentration gradient of ions with different diffusivity produces a local electric field triggering colloidal particles' motion in the solution through electrophoresis. Simultaneously, the

concentration gradient of ions creates an osmotic pressure gradient along the particle's surface, which contributes to the colloidal particles' motion through chemiphoresis resulting in particle propulsion towards the higher or lower concentration of ions [57], [58]. The direction of particles' motion in the concentration gradient depends on the surface charge of the particles, the sign and magnitude of the local electric field, and the interaction of particles with solute molecules which can be attractive or repulsive.

Most recent studies have used ion-exchange membranes such as Nafion in a microfluidic channel to generate the exclusion zone [31], [52], [88], [110], [119], [126]. Ion-exchange membranes create a gradient of ions, which in turn causes the colloidal particles to repel from the membrane surface and form the exclusion zone in the channel. In these systems, a combination of larger cations (typically Na^+ or K^+) and smaller cations (H^+) is present, complicating the description of local ion and charge distributions.

In this work, we utilize a dead-end pore geometry and we benefit from the interfacial chemistry of the microfluidic device to create a self-generated concentration gradient of ions. In the past decade, a dead-end pore geometry was the prevalent configuration to generate concentration gradients in microfluidic chips to investigate diffusiophoretic transport at the microscale [29], [67], [69]. Although the concentration gradient generating procedure is entirely different in our system from Florea's work[31], physical principles in the formation of the exclusion zone are similar to their study. However, the only cation present is H^+ in our system, simplifying its physical understanding. We do not use any salt or other solute to generate the ionic concentration gradient, which is simply developed by the interfacial interaction between the PDMS wall and DI water.

We combine experimental observations and analytical investigation of the exclusion zone formation. A boundary layer model was developed to analytically calculate the exclusion zone thickness. We experimentally evaluated the exclusion zone thickness as a function of the particles' positions. Furthermore, we explore the transient dynamics of the exclusion zone in our system for two different sizes of silica particles. Our theoretical analysis is in good agreement with the experimental results demonstrating that the exclusion zone thickness is highly dependent on the Sherwood number.

3.2 Experimental setup

3.2.1 PDMS Microfluidic Channel

We perform experiments on a microfluidic chip with a design and dimensions as shown in Fig 3.1. We used a dead-end pore geometry that includes two sections, a main channel, and side channels which are referred to as pores.

The width and height of the main channel, respectively, are $300\text{ }\mu\text{m}$ and $90\text{ }\mu\text{m}$. The height and length of the dead-end pores are $30\text{ }\mu\text{m}$ and $1500\text{ }\mu\text{m}$, respectively. In our design, we considered 3 different values for the width of the pores which are $50\text{ }\mu\text{m}$ (w_{p1}), $100\text{ }\mu\text{m}$ (w_{p2}), and $150\text{ }\mu\text{m}$ (w_{p3}). The height of dead-end pores is thinner than the main channel to reduce the disturbance from the main channel inside pores[85]. Additionally, the narrow pore geometry (width $\ll$ length) allows for neglecting the pressure gradient in the y-direction[30], and considering a one-dimensional motion of colloidal particles in the x-direction. Therefore, this channel design provides a good condition to analyze the motion of colloidal particles under the influence of a transient one-dimensional concentration gradient[127].

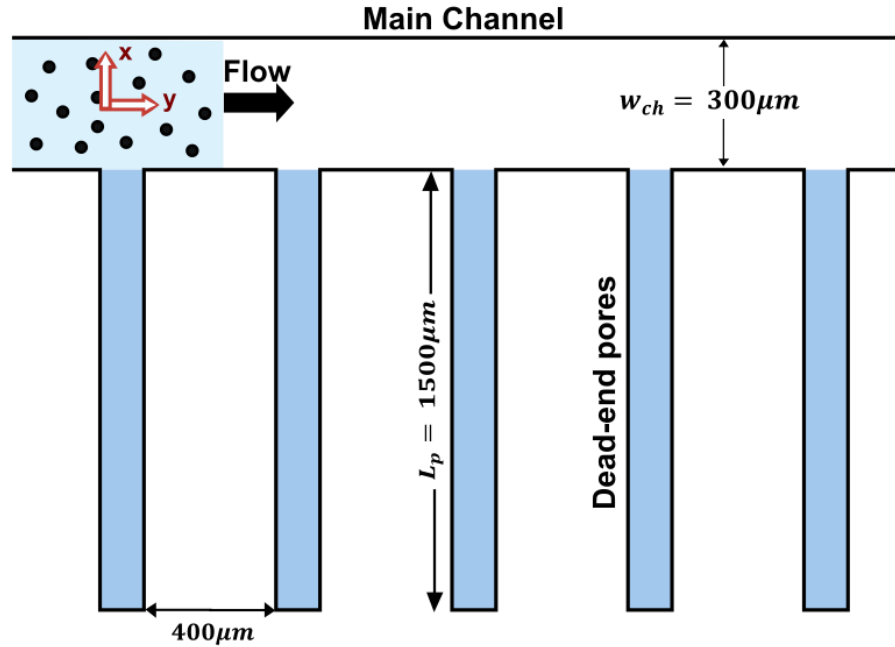


Fig 3.1 Schematic configuration of the dead-end pore geometry and dimensions. After filling pores with DI water, a suspension of silica particles flows through the evacuated main channel and reaches a series of dead-end pores containing DI water.

The PDMS channels are prepared by standard soft lithography procedures where the mixing ratio of the elastomer base (PDMS) and the curing agent (Dow Corning, Sylgard® 184) was 10:1. Subsequently, the mixture goes through a desiccation process in the vacuum desiccator to remove air bubbles. Then, we pour the mixture on the patterned master mold and heat it to 90 °C for 2 hours after the desiccation process. In the final step, we peel back the cast PDMS and plasma-bond it to a glass slide. We use the prepared channel for running every experiment after 24h.

3.2.2 Experimental Protocol

We prepared two suspensions of silica particles with different diameters, 1 μm , and 2 μm (SOLADTM particle, Glantreo) suspended in DI water at the volume fraction of 2.6×10^{-4} to ensure that we are in the dilute concentration. We use a bath sonicator for 20 min to suspend silica particles in DI water. We initially inject pure DI water without particles into the chip using a syringe pump (Harvard Apparatus). Once both the main channel and pores were filled, we introduced an air bubble into the main channel which is followed by the second solution containing colloidal suspension in DI water with a flow rate of 250 $\mu\text{L/h}$. When the colloidal particle suspension reaches the entrance of the first pore, the mean flow rate is reduced to 30 $\mu\text{L/h}$.

We start recording videos as soon as the colloidal suspension (second solution) reaches the entrance of the first pore. Observations were made at 10 $\times$ magnification for most cases using the ECHO microscope (RVL-100-G, San Diego CA, USA). General image processing is carried out in ImageJ.

3.3 Results and discussion

3.3.1 Exclusion Zone in the dead-end pore geometry

In our setup, charged silica particles ($\zeta_p = -37 \text{ mV}$) are suspended in DI water and based on the chemical equilibrium of water ($\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$) and dissolution of carbon dioxide in a solution exposed to the atmosphere the available ions in the solution are H^+ , OH^- , HCO_3^- , and CO_3^{2-} . The concentration of these ions in the pores is different from their concentration in the colloidal suspension due to the ions' interfacial interactions with channel walls in the pores which have a negative surface charge ($\zeta_{\text{PDMS}} = -49 \text{ mV}$ [128]).

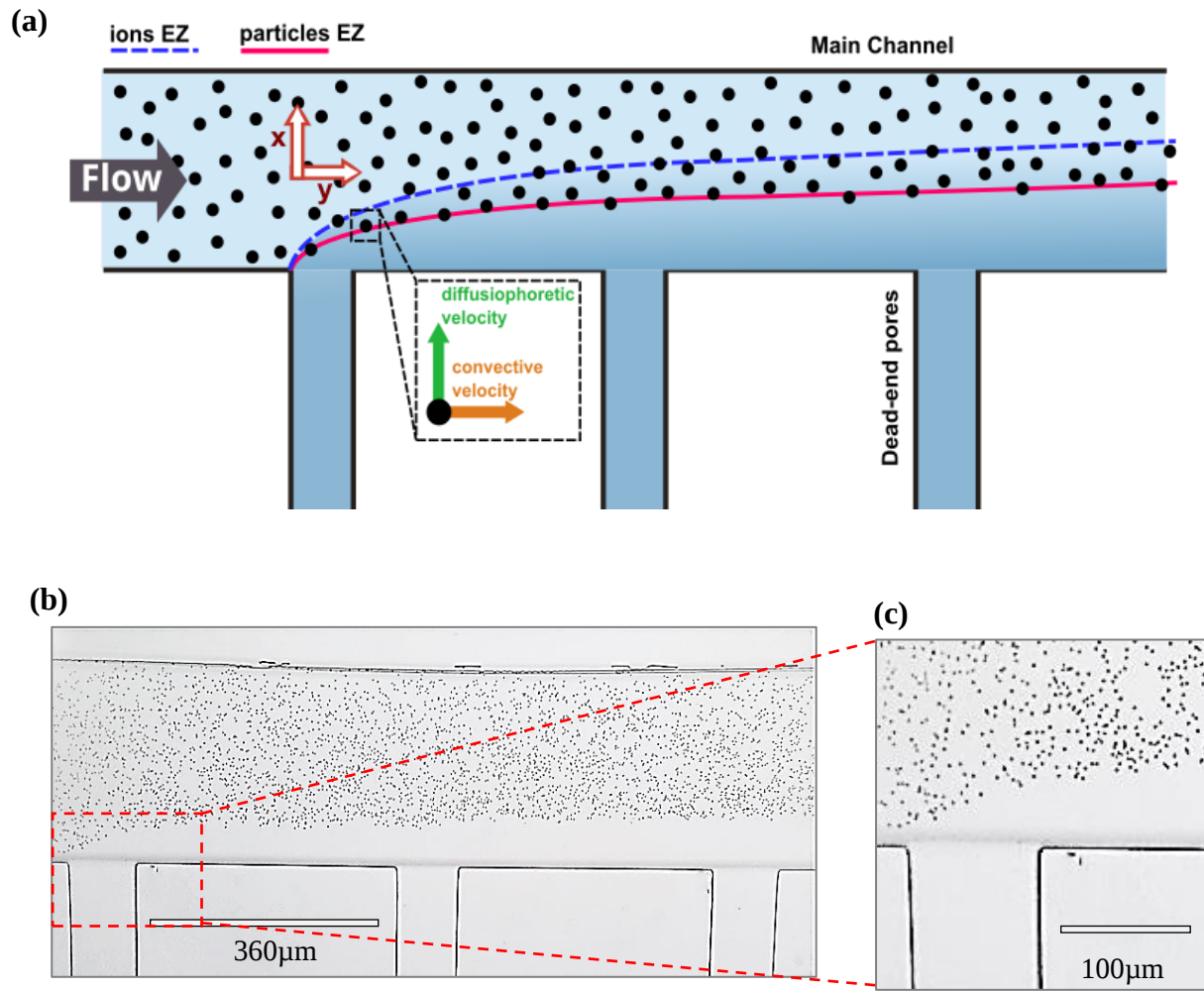


Fig 3.2 A schematic representation (a) and experimental observation (b) of the exclusion zone formation in the main channel caused by a self-generated concentration gradient from the dead-end pores. (a) The blue dashed line represents the ionic exclusion zone, which is larger than the particle exclusion zone represented by the red line. A particle in the main channel experiences forces in the tangential direction as a result of the ion concentration gradient. Experimental observation of the exclusion layer formation in the dead-end channel for pore width = 100 μm .

Therefore, as colloidal particles pass through the channel and reach the first pore, the concentration gradient of ions starts to develop through the pores into the main channel. As a result, the suspended particles tend to migrate away from the pores of the channel over time as shown in Fig 3.2 (also see Appendix A), and a temporary arc-shaped exclusion zone is developed along the y-direction which is caused by ion diffusion and ion concentration gradient, together with a constant flow of colloidal suspension.

The formation of the exclusion zone by colloidal particles depends on the balance between diffusiophoretic velocity and convective velocity as displayed in Fig 3.2. The diffusiophoretic velocity of a particle ($\mathbf{U}_{DP}$) is proportional to the gradient of the logarithm of the ion concentration as [67]

$$\mathbf{U}_{DP} = D_{DP} \nabla \ln C \quad (3.1)$$

Where $C(\mathbf{x},t)$ is the solute concentration as a function of position and time and D_{DP} is the diffusiophoretic mobility of particles which in the case of a thin Debye layer (Debye length $\ll$ radius of the particle) and symmetric electrolytes is defined as [67]

$$D_{DP} = \frac{\varepsilon k_B T}{\mu z e} \left[\frac{D_+ - D_-}{D_+ + D_-} \zeta_p + \frac{4 k_B T}{z e} \ln \left(\cosh \left(\frac{z e \zeta_p}{4 k_B T} \right) \right) \right] \quad (3.2)$$

Where ε is the electrical permittivity of the solution, k_B is the Boltzmann constant, T is the absolute temperature, μ is the viscosity of the solution, z is the valence of the ions, e is the elementary charge, ζ_p is the zeta potential of particles, D_+ is the cation diffusivity, and D_- is the anion diffusivity. Furthermore, based on eq (3.1), the diffusiophoretic velocity depends on $\nabla \ln C$, implying that only relative changes in the solute concentration affect the diffusiophoretic velocity, and even at extremely low solute concentrations, the diffusiophoresis phenomenon can cause the formation of exclusion thickness[31]. The convective velocity can be adjusted by changing the inlet flow rate to the main channel. In the following, theoretical analysis and experimental results of the formation of the exclusion zone are discussed.

3.3.2 Ion's boundary layer analysis

The available ions present in our system are H^+ , OH^- , HCO_3^- , and CO_3^{2-} , as a result of the interactions of DI water with the PDMS walls. When multiple ions are present in the system, predicting the ion concentration profile analytically by using the diffusion-advection equation is difficult due to coupling in ion concentrations. Four Nernst-Planck equations should be written for each of these ions separately. If the local electroneutrality, the chemical equilibrium of water, and the second chemical equilibrium of CO_2 dissolution ($HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$) are satisfied, these four equations can be reduced to one equation for the ionic pair $H^+ - HCO_3^-$. These ions can

create a large diffusion potential due to the large difference in their diffusivities ($D_{H^+} = 9.3 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ and $D_{HCO_3^-} = 1.2 \times 10^{-9} \text{ m}^2\text{s}^{-1}$) based on the first term in eq (3.2)[111]. The simplified Nernst-Planck equation relates the concentration of the H^+ to its diffusion flux and the background flow velocity as [31], [110], [129]

$$\frac{\partial c_H}{\partial t} = \nabla \cdot (D_{Heff} \nabla c_H - \mathbf{u} c_H) \quad (3.3) \quad D_{Heff} = \frac{2D_H D_{HCO_3}}{D_H + D_{HCO_3}} \quad (3.4)$$

Where $\mathbf{u}$ is the background flow velocity, c_H is the concentration of H^+ and D_{Heff} is the effective diffusivity that can be obtained through eq (3.4). The governing boundary conditions in our system are:

$$c_H = c_{H\infty} \text{ at } y = 0 \text{ (inlet)} \quad (3.5)$$

$$\mathbf{n} \cdot (-D_H \nabla c_H + \mathbf{u} c_H) = \mathbf{n} \cdot (\mathbf{u} c_H) \text{ at } y = L_{ch} \text{ (outlet)} \quad (3.6)$$

$$\frac{dc_H}{dx} = 0 \text{ at } x = \frac{w_{ch}}{2} \quad (3.7)$$

Where $c_{H\infty}$ is the bulk H^+ concentration in the main channel, $\mathbf{n}$ is the outward normal vector, and L_{ch} is the channel length. Applying the ‘boundary layer theory’ as shown in Appendix A, the exclusion zone thickness can be obtained as follows

$$\delta = \sqrt{\frac{8 D_{Heff}}{3 \bar{u}_y}} y \quad (3.8) \quad \rightarrow \quad \delta = w_{ch} \sqrt{\frac{8}{3} \frac{1}{Sh} \frac{y}{L}} \quad (3.9)$$

Where Sh is the Sherwood number representing the ratio of longitudinal convective transfer to the transverse diffusion rate which links most of the physicochemical parameters (flow rate, diffusivity of ions, and geometrical factors) of the system.

$$Sh = \frac{w_{ch}^2 \bar{u}_y}{D_{Heff} L} \quad (3.10)$$

Hence the only non-geometrical parameter that controls the problem and thus, Sh, is the mean flow velocity. As the mean flow velocity increases, the migration of ions is dominated by the convective velocity and the boundary layer of ions perpendicular to the flow direction is smaller causing a smaller exclusion zone[130].

3.3.3 Particles' trajectory analysis

As explained in the previous section, colloidal particles are moving in the main channel based on the balance between diffusiophoretic force, convective drag, and Brownian force. In our system, the particles' velocity in the x-direction is dominated by diffusiophoretic velocity, and the particles' velocity in the y-direction is dominated by convective velocity. In these assumptions, the exclusion zone for colloidal particles based on their trajectory is the following formula in the limit of steady state (see SI section A3 for more detail)

$$\delta_p = \frac{D_{DP}}{C_{H\infty}} C_{H0} \sqrt{\frac{2}{3} \frac{1}{D_{Heff} \bar{u}_y}} y \quad (3.11)$$

Eq (3.11) is a function of the bulk ion concentration in the pore and the bulk ion concentration in the main channel which cannot directly be measured experimentally. Fig 3.3 shows the experimental results multiplied by the square root of velocity for two different flow rates presenting the same results and verifying that eq (3.11) can accurately describe the main relevant physical mechanisms in our experiments. Also, the ratio of normalized particle exclusion thickness at two different flow rates is shown in figure A2 in Appendix A which shows a good agreement between theoretical and experimental results.

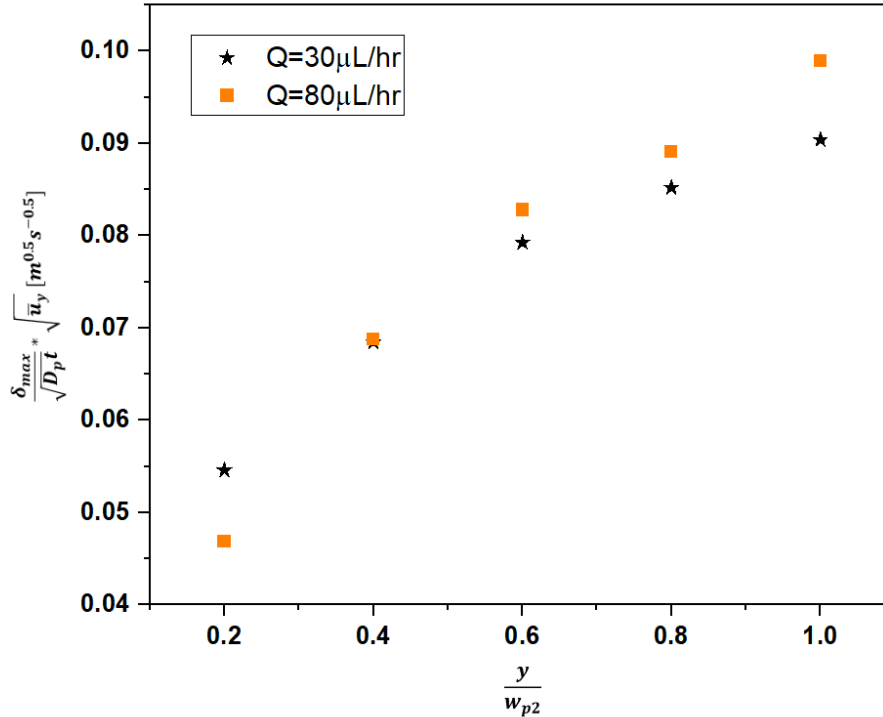


Fig 3.3 The experimental data of normalized particle exclusion thickness multiple by the square root of velocity for 2 μm silica particles. The orange square shows experimental data in $Q=80 \mu\text{L/hr}$, and the black star is for 30 $\mu\text{L/hr}$. The pore width in this diagram is 100 μm .

Besides, a comparison of experimental data with theoretical ions' migration for exclusion zone thickness is shown in Fig 3.4 using eq (3.9). For different pore widths (w_p), the theoretical predictions are qualitatively similar to experimental observations. The particle exclusion zone is slightly smaller than the predicted ionic gradient zone, which is in line with expectations.

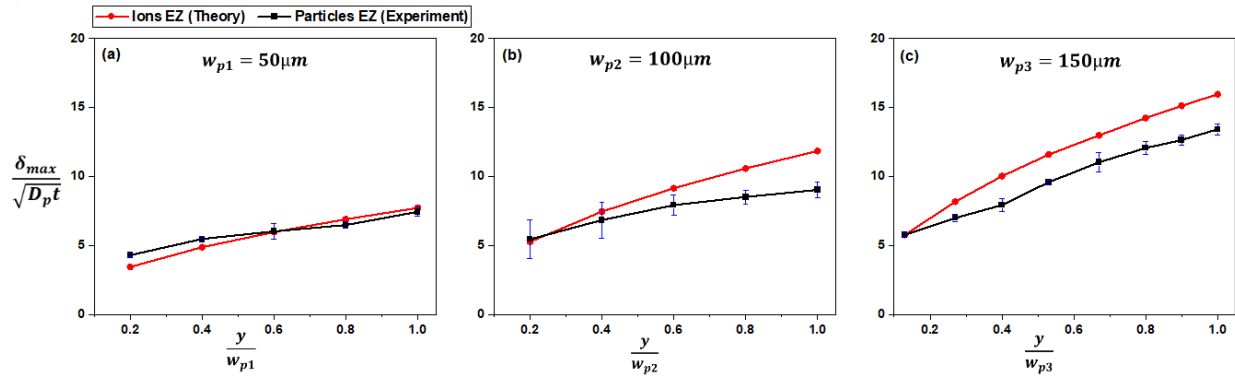


Fig 3.4 Comparing the exclusion zone thickness as a function of position over the first pore calculated in theory with experimental results for 2 μm silica particles. (a) For pore width=50 μm . (b) For pore width=100 μm . (c) For pore width=150 μm . The red curve represents the ionic exclusion thickness and the black curve displays the silica particles exclusion thickness.

Using values of the physical parameters in our system to determine the diffusiophoretic mobility, we find $D_{DP} = 6.19 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (eq (3.2)), which is orders of magnitude larger than the expected diffusion coefficient for 2 μm silica particles in water calculated using the Stokes-Einstein equation; $D_p = \frac{k_B T}{6\pi\mu r} = 2.18 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. On the other hand, the migration of ions in a concentration profile depends on the effective diffusivity which is equal to $2.094 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (based on eq (3.4)) in our system. Thus, the effective diffusivity for ions is larger than the particles' diffusiophoretic mobility which gives rise to generating the larger ion exclusion thickness in theory compared to the experimental results for particles as presented in Fig 3.4.

It is worth mentioning that a substantial factor that can affect the diffusiophoretic mobility value is the zeta potential of colloidal particles as shown in eq (3.2). Lee et al. [110] have presented that when the magnitude of the zeta potential of colloidal particles (ζ_p) is larger, suspended particles will be excluded further away from the ion-exchange membrane and tend to form a larger exclusion zone in the channel because the diffusiophoretic velocity is stronger to initiate the formation of an exclusion zone. In our system, the zeta potential of silica particles was -37 mV approximately which confirms the difference between the particles' exclusion zone and boundary layer analysis prediction shown in Fig 3.4 based on Lee's results [110].

The thickness of the exclusion zone presented in Fig 3.4 is comparable with previous studies that utilized salt and ion exchange membrane to create an exclusion zone [110]. While in our setup, we do not use any salt or membrane to generate the concentration gradient. This is solely generated due to the geometry of the channel and the interfacial interaction of species with the channel wall, indicating that these interactions can have a significant influence on colloidal transport. In our experiments, the development of the exclusion zone in the main channel stops after the self-generated ion concentration gradient disappears ($t \sim 90$ s) indicating that at initial experimental times, this interfacial effect is non-negligible.

3.3.4 Evolution of the Exclusion zone

An advantage of the dead-end pore geometry is the possibility to study the kinetics behind the exclusion zone formation. The exclusion zone shown in Fig 3.2 diminishes after the ion concentration gradient fades due to the balance between the pores and the main channel. This means that the formation of the exclusion zone in the main channel is temporary because pores contain a finite amount of ionic species through the wall-fluid interactions which create this temporary concentration gradient in the channel. Measurements of the exclusion zone thickness as a function of time are presented in Fig 3.5 and Fig 3.6 for 2 μ m and 1 μ m silica particles, respectively. The exclusion zone thickness shown in Fig 3.5 and Fig 3.6 was normalized by the diffusion displacement. As the concentration gradient reduces over time, the exclusion zone thickness shrinks as well because the magnitude of diffusiophoretic velocity decreases.

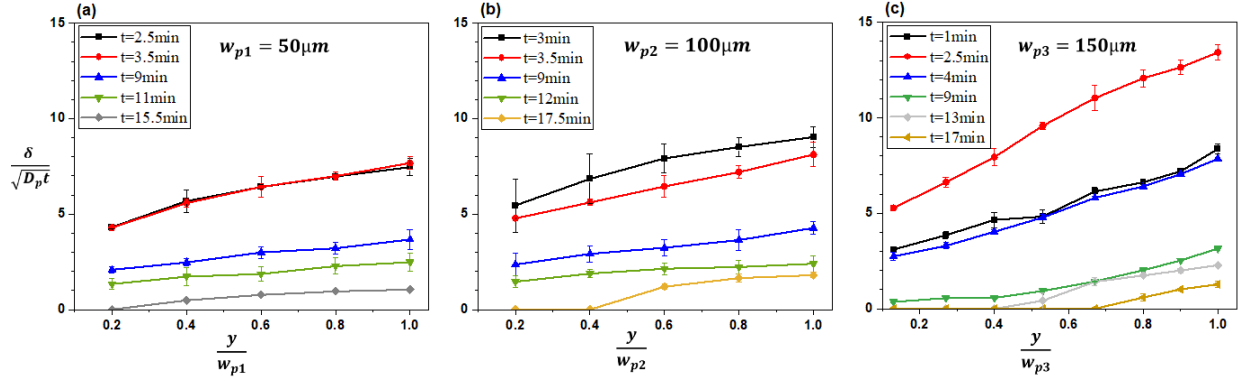


Fig 3.5 Normalized exclusion zone thickness over time for 2 μ m silica particles. (a) For pore width=50 μ m. (b) For pore width=100 μ m. (c) For pore width=150 μ m.

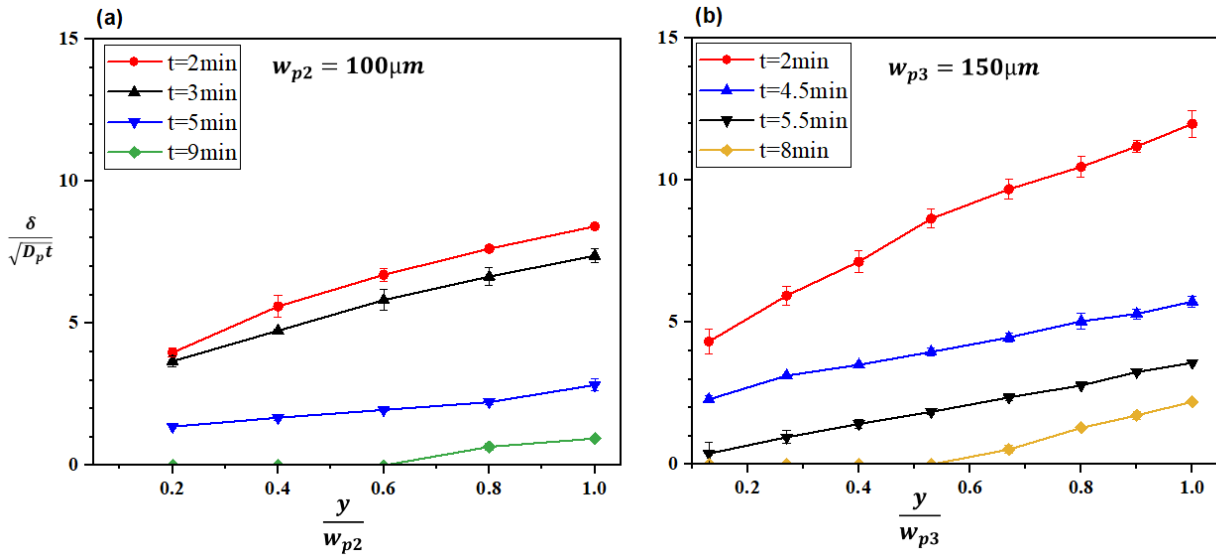


Fig 3.6 Normalized exclusion zone thickness over time for 1 μ m silica particles. (a) For pore width=100 μ m. (b) For pore width=150 μ m.

Both Fig 3.5 and Fig 3.6 show that the ratio of exclusion zone thickness to the diffusion displacement diminishes over time which means that the movement of silica particles in the x-direction is getting dominated by Brownian motion gradually due to the dwindling of ion concentration profile. In Fig 3.5(c), an increase in the exclusion thickness in the first few moments ($t=1$ min and $t=2.5$ min) and decreasing after reaching the maximum exclusion thickness (at $t=2.5$ min) can be observed. Although the exclusion zone thickness created in our system is comparable

with previous studies, the stability of the generated exclusion zone is limited because the ionic concentration profile is temporary and there is no renewal of the gradient in our system.

Moreover, the results for different pore widths shown in Fig 3.5 and Fig 3.6 indicate that the width of pores does not influence the transient evolution of the exclusion zone significantly because the number density of ions available in the pores does not change. The number density of ions is the key parameter controlling the stability of the exclusion zone which is constant for all three widths of pores. Thus, altering the width of pores between 50 μm and 150 μm does not affect the stability of the concentration gradient in the main channel which is in line with expectation as the number density of ions is constant in the pores.

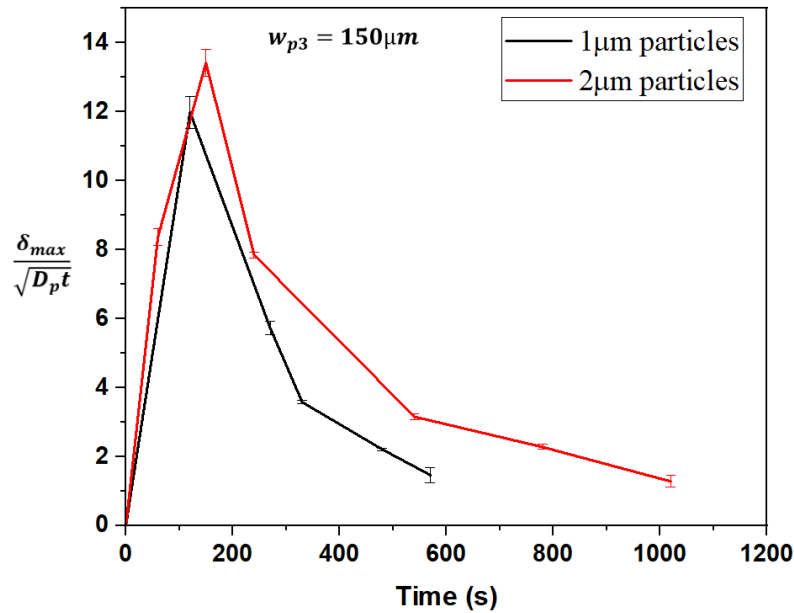


Fig 3.7 Effect of the particle size on the sustainability of the exclusion zone over time. This figure is plotted for the end-point ($y = 150\mu\text{m}$) of the first pore. The red curve and black curve represent $2\mu\text{m}$ and $1\mu\text{m}$ particles, respectively.

The exclusion zone's transient is different for 2 μm and 1 μm silica particles as shown in Fig 3.7. Both sizes of silica particles need almost the same time to reach the maximum exclusion zone thickness (~ 140 s); however, after reaching the maximum point, reduction in the exclusion zone thickness happens faster for 1 μm silica particles sample compared to 2 μm particles. This is because the diffusion coefficient of 1 μm particles ($D_p = 4.36 \times 10^{-13} \text{m}^2 \text{s}^{-1}$) is two times

higher than the one for 2 μm particles and accelerates the dwindling of the exclusion zone. As a result, the exclusion zone over the pore diminishes in a shorter time in the case of 1 μm silica particles ($\sim 600\text{s}$) in comparison with 2 μm silica particles ($\sim 1050\text{s}$). This indicates that the size of silica particles is an important factor in the transient dynamics of the exclusion zone.

3.3.5 Balance between diffusiophoretic velocity and convective velocity

As mentioned before, the establishment of the exclusion zone in the main channel depends on the net balance between diffusiophoretic velocity and convective velocity. Fig 3.8 demonstrates the influence of flow rate on exclusion zone thickness for three different injecting flow rates. A higher flow rate results in a higher Sh which triggers shrinkage in the exclusion zone thickness because it boosts the longitudinal convection. This behavior was experimentally observed as well; as we increased the flow rate from 30 $\mu\text{L/hr}$ to 80 $\mu\text{L/hr}$, the exclusion zone thickness formed by particles reduced as shown in Fig 3.8(a).

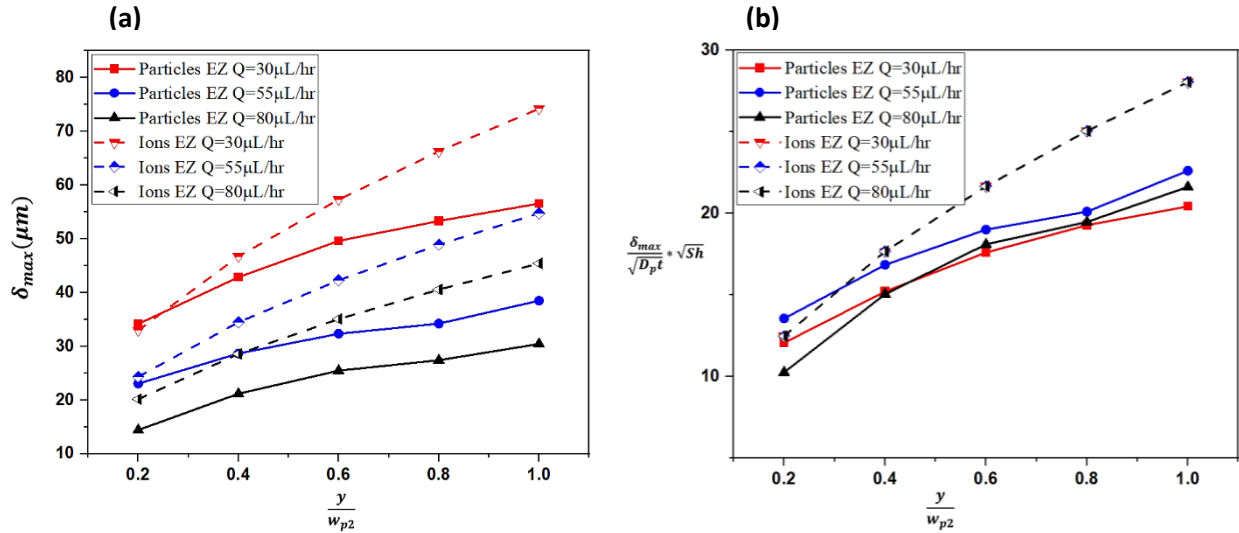


Fig 3.8 Effect of increasing flow rate on the maximum exclusion thickness based on the theoretical calculations and experimental observations for three different flow rates. The pore width in this diagram is 100 μm . Dashed lines show the ionic exclusion thickness and solid lines represent 2 μm silica particles exclusion thickness. (a) maximum exclusion thickness for each flow rate. (b) Scaling the dimensionless exclusion thickness by the inverse of the square root of the Sh number.

Also, the exclusion zone thickness reduction, with increasing the flow rate, in the experimental observation is larger than the theoretical prediction due to the difference in the diffusiophoretic mobility and the effective diffusivity of ions ($\frac{D_{DP}}{D_{Heff}} \cong 0.3$). As the diffusiophoretic mobility of silica particles is less than the effective diffusivity of ions, the longitudinal convective effect would be more dominant causing a larger reduction in the exclusion thickness in experimental data compared to the theoretical analysis (eq (3.9)). Moreover, Fig 3.8(b) verifies the dependency of exclusion thickness on the inverse of the square root of Sh as eq (3.9). The dimensionless exclusion thickness scales with the inverse of the square root of the Sh number and the experimental and theoretical data for different flow rates collapse. This effect is in qualitative agreement with the findings of Lee et al. for different Sh numbers [110].

3.4 Conclusion

We investigated a temporary exclusion zone mechanism by a self-generated concentration gradient. In previous studies [31], [88], [110], an ion exchange membrane, such as Nafion, and an imposed concentration gradient were used to form an exclusion zone in a microfluidic channel. On the contrary, the exclusion zone in our system is generated using a dead-pore geometry and the interfacial chemistry of the microfluidic device. Most importantly, we do not use any salt in our system to generate the exclusion zone and it is developed by the interaction of the PDMS wall in the pores with DI water. The observation of such an exclusion zone in systems without the addition of any background electrolyte has significant implications for experiments done in PDMS chips. We show that the surface chemistry of the channel walls should be considered when investigating diffusiophoretic effects as this can induce significant exclusion zones.

Through experimental observations and theoretical predictions, we verified the dependence of the thickness of the exclusion zone in the main channel on the Sh number. The difference between the theoretical predictions for the exclusion zone and the experimental observations is explained by a significant difference in ionic and particle diffusion coefficients. The maximum thickness of the exclusion zone in our setup was in the range of 150 μm along the channel length which is comparable with previous studies[110]. The effect of the induced concentration gradient is observed in a relatively short time as a result of the limited amount of ions present in the pores,

meaning that the exclusion zone vanishes over time and the effect of the self-induced gradients is specifically significant at the initial stages of an experiment. Additionally, the particle size has an effect on the temporal stability of the depletion zone, indicating that the size of particles plays a key role in the transient dynamics of the exclusion zone. We find that the sustainability of the exclusion zone for 2 μm silica particles is longer than 1 μm silica particles due to the smaller diffusivity of 2 μm silica particles based on the Stokes-Einstein equation.

The results of this study suggest potential applications in the micro-scale separation of colloidal particles. This self-generated exclusion zone using dead-end pore geometry provides a low-cost, energy-efficient, and easy-portable solution in membrane-less water filtration.

Chapter 4

4 The diffusiophoretic motion of porous and non-porous silica particles in a dead-end pore microfluidic channel

In this chapter, we have studied the diffusiophoretic motion of non-porous and porous silica particles under an electrolyte concentration gradient. The aim is to, for the first time, experimentally study the diffusiophoretic behavior of porous particles. For this purpose, we compared the behavior of porous particles and non-porous particles with identical surface chemistry and in similar conditions to analyze the effective parameters controlling the phoretic motion of porous particles under an electrolyte concentration gradient. In contraction to the previous chapter, the influence of the PDMS interaction with the solution is negligible in the case of electrolyte concentration gradient as the concentration of the available ions in the aqueous solution is significantly higher than the ions created by dissolved CO_2 in water. While for the non-electrolyte concentration gradient, the effect of PDMS interaction with the aqueous solution can be important because in non-electrolyte the only effective phenomenon is chemiphoresis which is small compared to the electrophoretic contribution. The PDMS interaction with the aqueous solution can indeed create an electrophoretic contribution as discussed in chapter 3.

4.1 Introduction

Diffusiophoresis refers to the spontaneous motion of suspended particles driven by a solute concentration gradient. This phenomenon was first described by Derjaguin et al. for nonelectrolytes in the 1940s; then, the analysis was further extended for electrolytes by Anderson and Prieve in the 1980s [44]–[46]. The physical origin of this phenomenon for electrolytes can be broken down into two components: chemiphoresis and electrophoresis. Typically, the presence of a chemical gradient produces local osmotic pressure variations along a particle surface causing particles to move. Simultaneously, a gradient of anions and cations with different diffusivities develops a local electric field to maintain electroneutrality in the solution that drives charged particles into motion. Similar physics applies for non-electrolyte solely through the action of chemiphoresis [29], [57], [58], [127]. Diffusiophoresis has been utilized in many various

applications in recent years such as drug delivery, wastewater treatment, separation, enhanced oil recovery, and laundry detergency [50], [52], [54], [55], [110].

During the past decades, the diffusiophoretic motion of charged non-porous particles has been investigated in a wide range of theoretical, numerical, and experimental aspects [131]–[134], [84], [68], [30], [29]. The diffusiophoretic velocity of a non-porous particle in a Newtonian fluid is defined as[58]

$$\mathbf{U}_{DP} = D_{DP} \nabla \ln C \quad (4.1)$$

Here, $C(\mathbf{x},t)$ is the solute concentration as a function of position and time and D_{DP} is the diffusiophoretic mobility of particles which in the case of a thin Debye layer (Debye length $\ll$ radius of the particle) and symmetric electrolytes, is given by[67]

$$D_{DP} = \frac{\varepsilon k_B T}{\mu z e} \left[\beta \zeta_p + \frac{4 k_B T}{z e} \ln \left(\cosh \left(\frac{z e \zeta_p}{4 k_B T} \right) \right) \right] \quad (4.2)$$

In this equation, ε is the electrical permittivity of the solution, k_B is the Boltzmann constant, T is the absolute temperature, μ is the viscosity of the solution, z is the valence of the ions, e is the elementary charge, ζ_p is the zeta potential of particles, and $\beta = \frac{D_+ - D_-}{D_+ + D_-}$ is the relative ratio of the diffusivities of cations (D_+) and anions (D_-) in the solution. The first term in eq (4.2) corresponds to the electrophoresis origin and the second term originates from chemiphoresis [67].

Diffusiophoresis of other charged colloidal entities such as porous particles has been explored in limited studies theoretically and numerically [39], [43], [40], [41]. Charged porous particles such as proteins, DNAs, porous silica, etc are important materials in various applications such as drug delivery, wastewater treatment, and separation[135], [136]. Also, diffusiophoresis occurs very often in these applications where charged non-porous or porous particles are present in these systems. In general, the migration of porous particles is faster than non-porous particles as a result of two effects. First, the porosity of porous particles with fully interconnected pores reduces the overall hydrodynamic drag force felt by porous particles because the suspending medium can flow through the particle to some degree which causes in increasing the particles' velocity in the solution[38], [41], [43]. Second, the fixed charges on the surface of porous particles are distributed all over the entire interior pore area of the particle creating a large electric driving force to attract

more counterions into the particle interior which can influence the nominal charge of porous particles[38], [42]. In the past decade, various numerical studies have shown that with increasing the porosity of porous particles, the diffusiophoretic velocity of particles increases as well. Also, the effect of double-layer thickness, fixed charges on the surface of porous particles, and the relative ratio of the diffusivities of ions (β) on the diffusiophoretic mobility has been investigated theoretically [38], [41], [43]. The diffusiophoretic velocity for porous particles is obtained as[43]

$$\mathbf{U}_{DP} = \frac{\varepsilon}{\mu} \frac{|\nabla C|}{C_0} \left(\frac{kT}{Ze} \right)^2 [(\kappa a)^2 \beta A_1 \bar{Q} + (\kappa a)^4 A_2 \bar{Q}^2] + O(\bar{Q}^3) \quad (4.3)$$

Where ε is the dielectric permittivity, C_0 is prescribed electrolyte concentration, κ^{-1} is the Debye length, a is the radius of the colloidal particle, $\bar{Q} = \frac{ZeQ}{\varepsilon \kappa^2 kT}$ is a dimensionless fixed-charge density, A_1 and A_2 are functions of permeability, the volume fraction of particles, and the electrokinetic radius (κa). This is a solution to the linearized Poisson-Boltzmann equation where higher order terms are neglected $\sim O(\bar{Q}^3)$.

To the best of our knowledge, there is currently no experimental study on the phoretic motion of porous particles under a concentration gradient. In this work, we experimentally investigate the difference in the migration of charged porous silica particles and non-porous silica particles under a temporary concentration gradient in dead-end pore geometries as the first experimental study on this topic. We analyze the phoretic motion of porous particles under an imposed electrolyte concentration gradient to distinguish their diffusiophoretic behavior from non-porous particles. This will help in designing an efficient experimental setup to benefit from the useful properties of porous particles, the larger electric driving force and reduced hydrodynamic drag force, for different applications like sorting or delivering particles in micro-scale systems.

4.2 Experimental setup

4.2.1 PDMS microfluidic channel

We use a microfluidic chip with a configuration shown in Fig 4.1. We used a dead-end pore geometry which consists of two sections, the main channel, and pores. The width and the height of the main channel are 300 μm and 90 μm , respectively. The height, length, and width of pores are 30 μm , 1000 μm , and 50 μm , respectively. The narrow pore geometry (width $\ll$ length) allows

for neglecting the pressure gradient in the y-direction[30]. Additionally, the height of dead-end pores is thinner than the main channel to reduce the disturbance from the main channel inside pores[85]. Therefore, this channel design can be considered as a one-dimensional motion of colloidal particles in the x-direction under the effect of the transient concentration gradient.

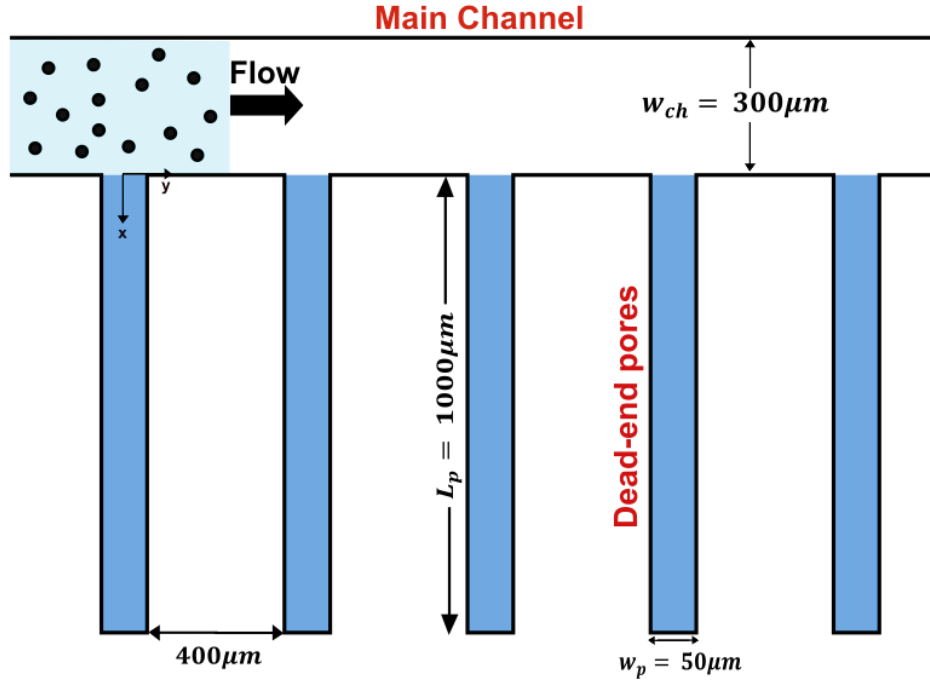


Fig 4.1 Schematic illustration of the dead-end pore geometry and dimensions. The pores are filled with solution 1 (electrolyte solution), then, solution 2 which is particle suspension in DI water is entered into the channel.

The PDMS channels are prepared using soft lithography procedures by mixing polydimethylsiloxane (PDMS) with a curing agent (Dow Corning, Sylgard[®] 184) in a ratio of 10:1 by weight. Subsequently, the mixture goes through a desiccation process in the vacuum desiccator to remove air bubbles inside the mixture. Then, we pour the mixture on a patterned silicon wafer mold and put the master mold in the vacuum desiccator to de-bubble it. Afterward, we put the master mold in the heater for 2 hours at 90 °C. In the final step, we peel back the cast PDMS and plasma-bond it to a glass slide.

4.2.2 Salt solutions and particle suspension

We used NaCl (Sigma-Aldrich) and NaOH (Sigma-Aldrich) salts in the experiments to create the concentration gradient of electrolytes. Initially, salts were dissolved in DI water to make 100 mM stock solutions; the solutions were further diluted to 10 mM for doing experiments.

We used 1 μm non-porous silica particles and 1 μm porous silica particles (SOLADTM particle, Glantreo) with two different pore sizes, 2 nm (BET surface area = 835.69 m^2/g), and 10 nm (BET surface area = 300.69 m^2/g). The silica particles are suspended in DI water using a bath sonicator for ~ 20 min at a concentration of 2.6×10^{-4} by volume (dilute regime of concentration).

The zeta potential of particle suspensions is measured using a Zetasizer nano (Malvern). The measurements are carried out using the commercial software provided by Malvern.

4.2.3 Experimental protocol for microfluidic channel

All the channels are used after 24 h of plasma-bonding it to a glass slide to minimize the effects of changes in PDMS surface properties[137]. In each experiment in the microfluidic channel, we initially inject the 10 mM salt solution by using a syringe pump (Harvard Apparatus) into the channel. Once it has filled the main channel, we block the outlet and apply gentle pressure to gradually fill the pores. After filling all pores with salt solution, the plug blocking the outlet is removed and the main channel is evacuated by introducing an air plug. Then, the particle suspension is flown through the main channel with a flow rate of 250 $\mu\text{L}/\text{h}$. As the particle suspension reaches the entrance of the first pore, the rate of injection is reduced to 30 $\mu\text{L}/\text{h}$. The particles are visualized with an inverted microscope (ECHO, RVL-100-G, San Diego CA, USA) at 20 $\times$ magnification and their motion is recorded under the microscope for almost 600 s. General image analysis is carried out in ImageJ.

4.2.4 Experimental protocol for drag force measurement

To study the hydrodynamic drag force difference between non-porous and porous particles, we measured the drag force of 2 μm non-porous silica particles and 2 μm porous silica particles (SOLADTM particle, Glantreo) with a pore size of 2 nm (BET surface area = 1221.7322 m^2/g) and 100 nm (BET surface area = 24.711 m^2/g) using an optical tweezers instrument (Tweez 305, Aresis). Not that these are different particles than the particles used for the dead-end pore experiments. The silica particles are suspended in DI water using a bath sonicator at a very dilute regime (less than 10^{-5} volume fraction). Then, we put a small volume of particle suspension on a

block area created by paraffin on a microscope slide and cover it with a coverslip. The measurements are done with a trap with a total strength of 0.1. Afterward, the drag force is measured by exerting different constant velocities on the particle in the range of 0 to 20 μms^{-1} .

4.3 Results and discussion

4.3.1 Drag force measurement using optical tweezers

As mentioned earlier, the hydrodynamic drag force is reduced for porous particles due to their permeability of the fluid through the interior pore area[38]. In our setup, the measured drag force of charged porous and non-porous silica particles ($\zeta_p = -37 \text{ mV}$) using an optical tweezers instrument is shown in Fig 4.2. We investigate the effect of surface area on drag force by measuring the drag force for porous silica particles with two different pore sizes ($P1=2 \text{ nm}$, $P2=100 \text{ nm}$) and non-porous silica particles. Stokes' drag force equation for non-porous particles verifies the obtained drag force for non-porous silica particles as follows

$$\mathbf{F} = 6\pi\mu a\mathbf{V} \quad (4.4)$$

Where μ is the fluid viscosity which is the viscosity of DI water at 22 °C ($0.00095 \text{ kg.m.s}^{-1}$) in this study as the particles' concentration is in the dilute regime, a is the particle radius, and $\mathbf{V}$ is the exerted velocity on the silica particle. In Fig 4.2, the experimental slope for non-porous silica particles is 0.0192 mg/s which shows a good agreement with the theoretical slope using eq (4.4) (0.018 mg/s) having a relative error of less than 7 percent.

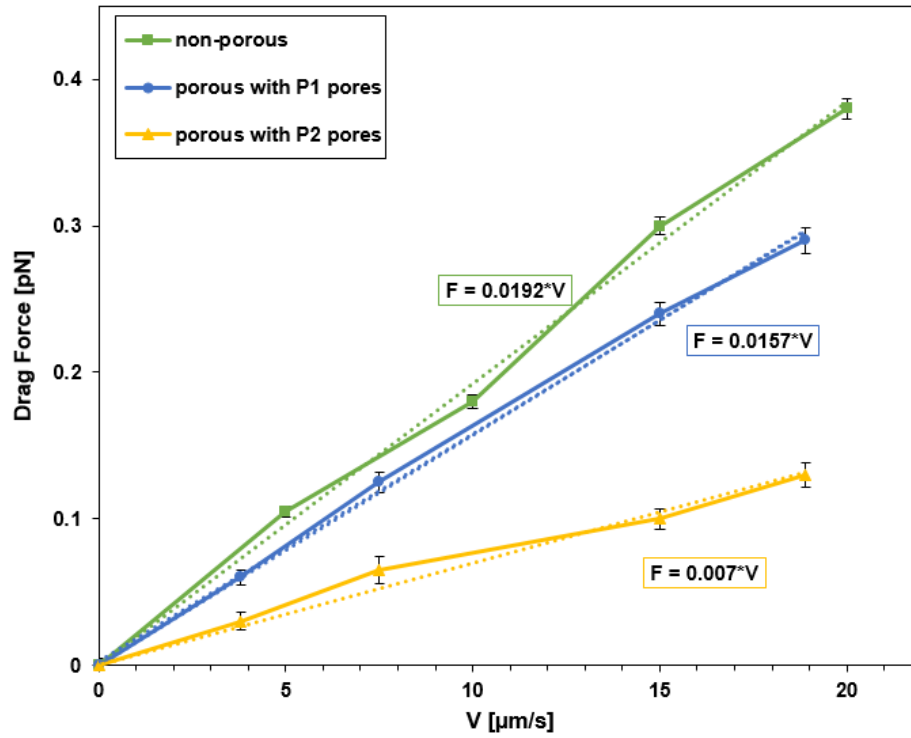


Fig 4.2 Drag force of 2 μm non-porous silica particles and porous silica particles as a function of velocity using the optical tweezers. Linear fits to represent Stokes' law are included (dashed lines). Also, the effect of the ratio of pore size to water molecule size is presented. The green line represents the non-porous drag force where the ratio of pore size to water molecule size is zero. The blue line represents 2 μm porous particles with 2 nm pores where the ratio of pore size to water molecule size is 7.4. The yellow line shows 2 μm porous particles with 100 nm pores where the ratio of pore size to water molecule size is 370.

As can be seen in Fig 4.2, the drag force decreases significantly with increasing the pore size from 2 nm to 100 nm. The drag force of particles with larger pores is 50% less than the small-pore particles and approximately 65% less than non-porous particles. Although the surface area of the particles with small pores is significantly larger than that of the large pore particle, the overall drag force of the small pores is larger compared to the particles with bigger pores, which is in line with expectations. We postulate this behavior arises from the ratio of pore size to water molecule size because it can affect the permeability of the fluid through the interior region of porous particles. Therefore, the pore size is more effective than the available surface area in changing the permeability in our experiments.

As the ratio of pore size to water molecule size increases from 7.4 to 370, the drag force reduces by 50 percent as shown in Fig 4.2. This represents the ratio of the particle's pore size to the solute molecule is a key parameter affecting the permeability and the overall hydrodynamic drag force. This ratio for the particles with 2 nm pores is 7.4 which is closer to the non-porous particles than the particles with 100 nm pores where the ratio is 370. The difference in the drag force of the particles with 2 nm pores with non-porous particles' drag force is almost 18%.

4.3.2 Diffusiophoretic motion of non-porous particles

To study the effect of the interior structure of colloidal particles on the diffusiophoretic motion of particles, we use a dead-end pore geometry to create a temporary concentration gradient in the pores. As shown in eq (4.2), β and particles' zeta potential are the effective parameters to change the diffusiophoretic mobility of non-porous particles. Both β and ζ_p can be positive or negative based on the available ions in the solution and the particle surface charge. Considering the attractive interaction between the particle and the solute molecule in our system, when $\beta\zeta_p > 0$, non-porous colloidal particles migrate toward higher electrolyte concentration. Otherwise, non-porous particles tend to move along lower concentrations of electrolyte. In our work, β for sodium chloride and sodium hydroxide solution is negative meaning that negatively charged non-porous particles are expected to move toward the higher solute concentration as shown in Fig 4.3.

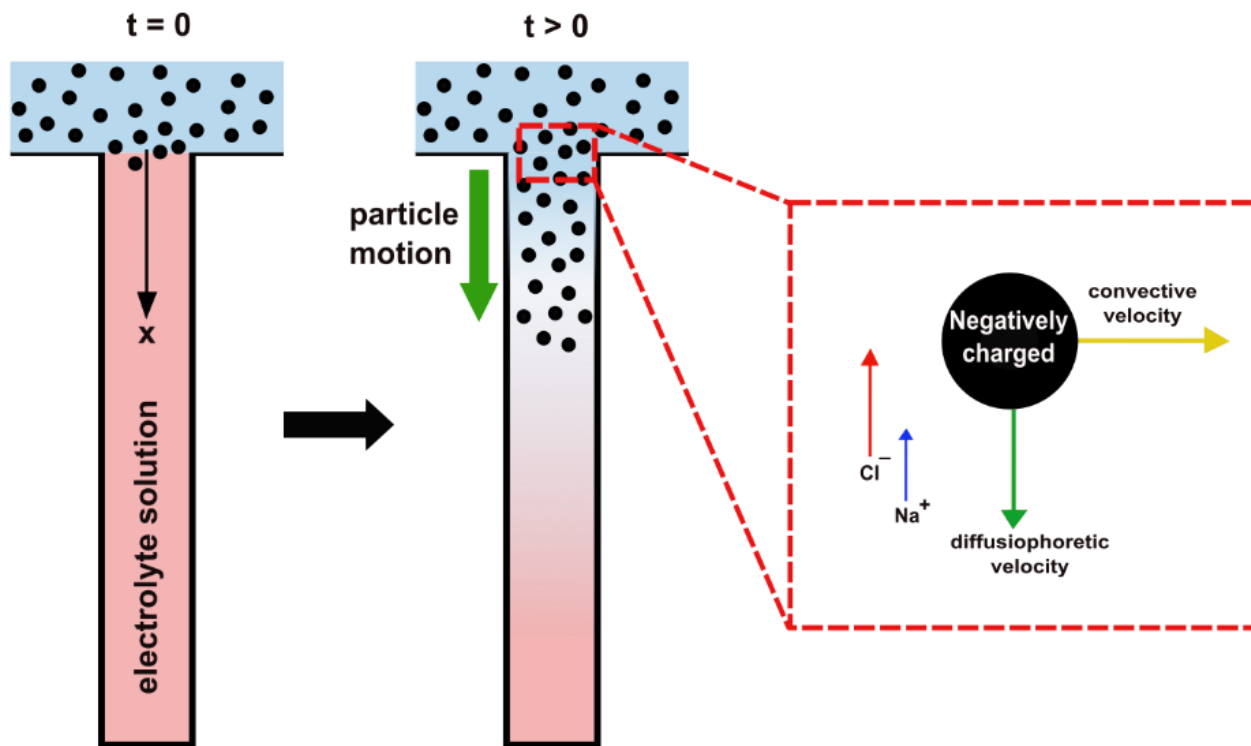


Fig 4.3 Schematic illustration of negatively charged particles under the electrolyte concentration gradient. In this figure, the pore is filled with the electrolyte which the diffusivity of negative ions is higher than positive ions, and the particle suspension without any electrolyte is passing over the entrance of the pore. At the starting point ($t = 0$), the particles just reach the entrance of the pores. After reaching the entrance of the pore, they will migrate toward the inside of the pore under the influence of electrolyte concentration gradient. The mechanism happening at the entrance of the pore around the negatively charged particle is shown in the right hand side for the NaCl electrolyte as an example, where the slower effective motion of Na^+ results in an electric field that drives the negatively charged particles into the pore.

Moreover, a salt with higher β induces faster diffusiophoretic motion of non-porous particles, according to eq (4.2). As β increases, both the electrophoretic term and the chemiphoretic term increase resulting in enlarging the diffusiophoretic mobility. In Fig 4.4 (a) & (b), the migration of charged non-porous silica particles under the concentration gradient of NaCl (10mM, $\beta = -0.21$) and NaOH (10mM, $\beta = -0.6$) is shown, respectively.

As we expected, the non-porous silica particles in both electrolytes are moving into the pores over time due to the diffusiophoretic velocity as illustrated in Fig 4.3. The net observed particle motion in the pores is a combination of diffusiophoresis and wall-driven diffusioosmosis. The diffusioosmotic flow of the aqueous phase is created along the pore walls because the channel walls (PDMS) are charged[30], [55], [67] which is in the negative x-direction to maintain the zero net mass flux condition in the pores. As the zeta potential of the PDMS wall increases, the diffusioosmotic velocity increases based on recent studies[138], [139]. Furthermore, the distribution of 1 μm non-porous silica particles at the maximum position in the pores is approximately parabolic in the 10 mM NaOH as is clearly shown in Fig 4.4(b); however, in Fig 4.4(a), the front of particles is nearly flat. The shape of the distribution at the front shows the effect of the diffusioosmotic velocity on the particles' migration. The maximum position is defined as the maximum location of migrated particles inside the pores where there are more than 1 percent of total particles are present in that location.

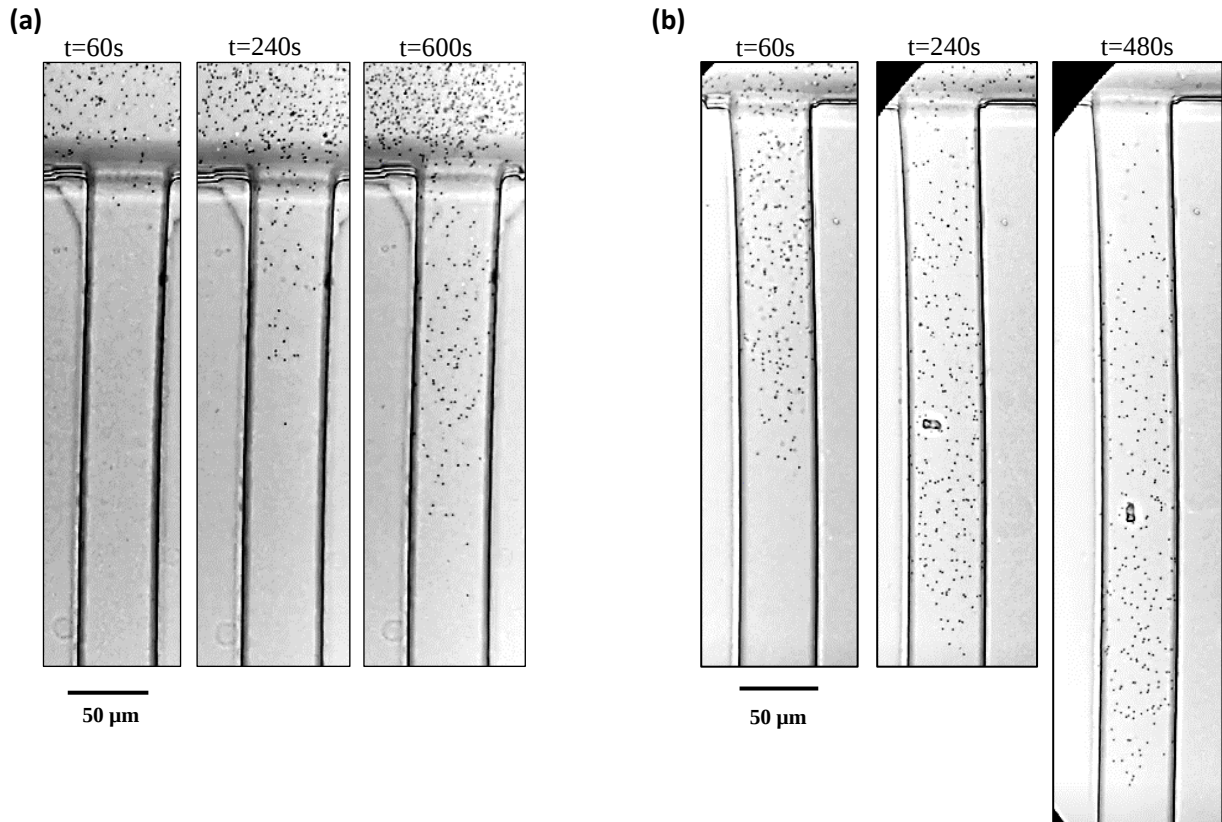


Fig 4.4 Entrainment of 1 μm non-porous silica particles into the pores in the presence of the electrolyte concentration gradient as a function of time. (a) Migrating of 1 μm non-porous silica particles under the NaCl concentration gradient. (b) The motion of 1 μm non-porous silica particles under the NaOH concentration gradient.

It can be observed that the diffusioosmotic velocity in the 10 mM NaOH (pH~12) solution is larger than the 10 mM NaCl (pH~7) solution which is in line with expectation as the magnitude of wall zeta potential in 10 mM NaOH is larger than the 10 mM NaCl solution.

The dimensionless maximum position of non-porous silica particles over time under the concentration gradient of NaCl and NaOH is displayed in Fig 4.5. The maximum position of particles is scaled by the entrance length of the pores. The entrance length can be defined as the length from the inlet of the pores where the flow is hydrodynamically developing inside the pores. An empirical equation for calculating the entrance length in a rectangular cross-section is[94]

$$L_e = w_{cs} \left(\frac{0.55}{1 + 0.13Re} + 0.065Re \right) \quad (4.5)$$

Where L_e is the entrance length, w_{cs} is the width of the cross-section and Re is the Reynolds number which is defined as $Re = \rho u w_{cs} / \mu$ for a rectangular channel in which w_{cs} is the larger side. In our setup, the entrance length is 27.5 μm using eq (4.5).

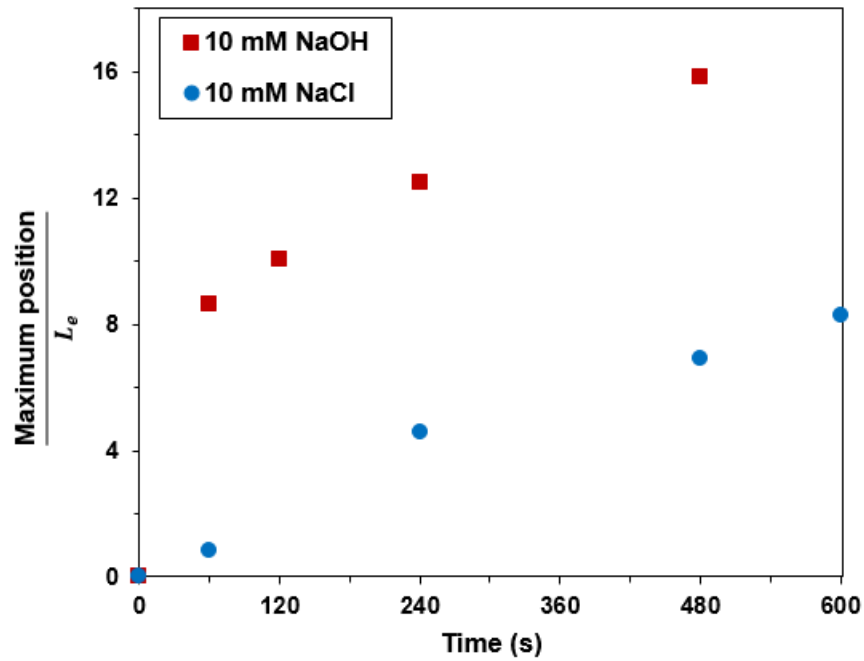


Fig 4.5 Dimensionless maximum position of 1 μm non-porous silica particles under the imposed electrolyte concentration gradient over time. The red squares and blue circles represent the influence of 10 mM NaOH and 10 mM NaCl, respectively.

As shown in Fig 4.5, the scaled maximum position of 1 μm non-porous silica particles under the concentration gradient of 10 mM NaOH is larger than the 10 mM NaCl case. This can be explained through the relative diffusivities of the ions, β , in the system according to eq (4.2). As β increases, the electrophoretic contribution increases as well resulting in higher diffusiophoretic mobility. The β value for NaCl and NaOH is -0.21 and -0.6, respectively, and thus it is expected that the particles move further in a NaOH concentration gradient when compared to the same NaCl concentration gradient.

Moreover, the presence of electrolytes influences the zeta potential of particles which is the second effective parameter in the diffusiophoretic mobility as shown in eq (4.2). The changes in the particle's zeta potential affect both the electrophoretic and chemiphoretic terms in eq (4.2). Based on the zeta potential measurements, the zeta potential of 1 μm non-porous silica particles in the 10 mM NaCl solution and 10 mM NaOH solution is -20.57 ± 1.91 mV and -98.43 ± 4.89 mV, respectively.

We calculate the diffusiophoretic mobility of 1 μm non-porous silica particles based on eq (4.2) using values of the physical parameters in our system which results in $D_{\text{DP, NaCl}} = 2.4 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ and $D_{\text{DP, NaOH}} = 12.3 \times 10^{-10} \text{ m}^2\text{s}^{-1}$. Therefore, the diffusiophoretic velocity in the 10 mM NaOH is approximately 5 times larger than 10 mM NaCl which leads non-porous particles to move faster and reach a larger maximum position compared to the 10 mM NaCl solution which is in agreement with experimental results shown in Fig 4.5. Also, these results are in line with Shim et al. study about the effect of zeta potential and electrolyte on the diffusiophoretic mobility[139]. The migration of non-porous particles into the pores is getting slower over time due to the reduction of the electrolyte concentration gradient inside the pores which decreases the diffusiophoretic motion.

4.3.3 Diffusiophoretic motion of porous particles

We visualize the diffusiophoretic motion of 1 μm porous silica particles with two different pore sizes (2 nm and 10 nm) under the same electrolyte concentration gradients as the non-porous particles. The observation for both samples of porous particles under the concentration gradient of 10 mM NaCl is shown in Fig 4.6. In Fig 4.6(a), the migration of 1 μm porous silica particles with 2 nm pore size shows that a very limited number of particles enter the pore compared to the same

condition for 1 μm non-porous silica particles (Fig 4.4 (a)). Also, for the particles with 10 nm pores, particles just enter close to the entrance of the pores over time as displayed in Fig 4.6(b), but they do not move further toward the inside of the pores. This expected behavior arises due to the two main effects. First, when the porous particle suspensions are in contact with the 10 mM NaCl at the entrance of the pores, the Debye layer is very thin ($\kappa^{-1} \sim 3 \text{ nm}$) which means κa is large (~ 160). When κa is large, the fixed charges carried by the porous particles can be neutralized by driving counterions into the interior region of porous particles. This phenomenon is called “counterion condensation” or “shielding effect” which causes porous particles to be chargeless and suppress the chemiphoretic contribution completely[38], [140]–[142]. Therefore, the second term in eq (4.3) will be zero. It should be noted that this behavior is in direct contrast to the behavior of non-porous particles for which the chemiphoretic contribution increases with increasing κa .

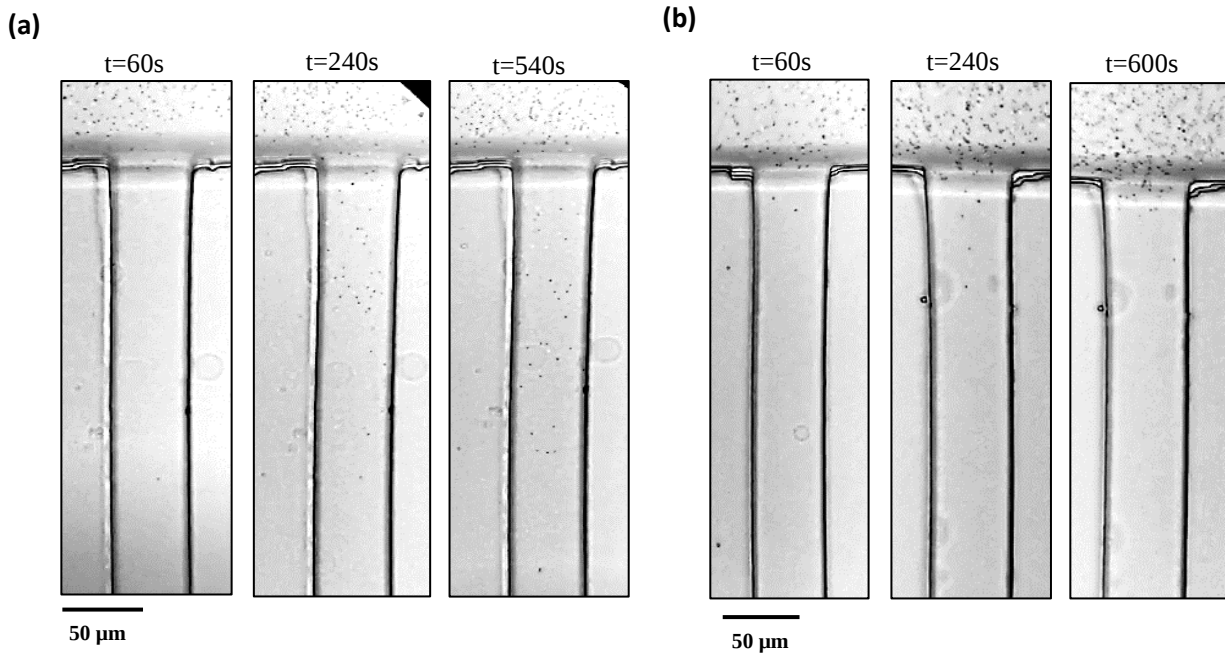


Fig 4.6 Diffusiophoretic motion of porous silica particles under the concentration gradient of 10 mM NaCl. (a) Time sequence images for 1 μm porous silica particles with 2 nm pores (b) Time sequence images for 1 μm porous silica particles with 10 nm pores.

Additionally, the diffusiophoretic mobility for porous particles as shown in eq (4.3) is a function of the dimensionless particle surface charge density. The measured zeta potential for 2 nm and 10

nm pore size particles in 10 mM NaCl is -22.66 ± 1.95 mV and -23.43 ± 0.9 mV, respectively. The surface charge density for a binary system can be determined using the Gouy-Chapman equation which relates the particle zeta potential to the surface charge density as shown below[143].

$$Q = \frac{2\epsilon k_B T}{\kappa^{-1} e} \sinh\left(\frac{e\zeta_p}{2k_B T}\right) \quad (4.6)$$

According to eq (4.6) and the dimensionless surface charge equation, the dimensionless surface charge for 2 nm and 10 nm pore size particles in 10 mM NaCl is -7.815×10^{-5} and -8.1×10^{-5} , respectively. The actual magnitude of the surface charge is higher than this amount because the zeta potential is measured at the slipping plane which has a lower electric potential than the surface. Based on recent studies, these values for surface charge density are very low[38]–[41], [43] resulting in near-zero diffusiophoretic mobility.

Second, the imposed velocities on the particles at the entrance of the pores in the x-direction and y-direction are diffusiophoretic velocity and convective velocity, respectively as represented in Fig 4.3. The reduced hydrodynamic drag force of the porous particles in the main channel causes the effect of convective velocity in the y-direction to increase.

As a result, the small value in the surface charge density creates a very small diffusiophoretic velocity, and the reduced hydrodynamic drag force in the main channel increases the particles' convective velocity in the main channel. The balance between these two velocities will be dominated by the convective velocity and porous particles tend to move in the main channel without being captured into the pores. For capturing porous particles inside the pores, the porous particles' dimensionless surface charge density should be larger than 0.01[41], [43].

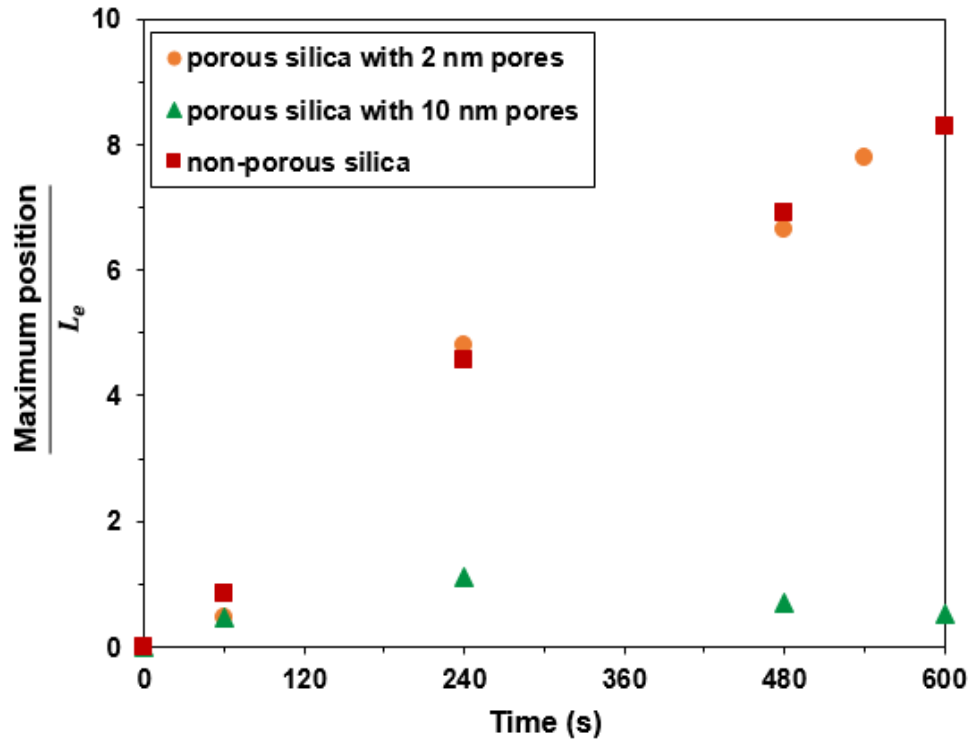


Fig 4.7 Scaled maximum position of 1 μm non-porous and porous silica particles under the 10 mM NaCl concentration gradient over time. The orange circles, green triangles, and red squares represent particles with pores of 2 nm, 10 nm, and non-porous particles respectively.

The scaled maximum position over time for porous particles with small 2 nm and 10 nm pores under the concentration gradient of NaCl is shown in Fig 4.7. In this figure, the scaled maximum position of particles with 10 nm pores does not exceed 1 over time. This means porous particles did not diffuse more than the entrance length into the pore and they are solely migrating by the hydrodynamic flow which creates vortices at the inlet of the pores. Also, a limited number of particles with 2 nm pores in 10 mM NaCl are moving inside the pores over time as shown in Fig 4.6(a). This behavior stems from the small pore size of porous particles which leads to behaving closer to non-porous particles in the solution which results in the migrating of some of the 2 nm pore size sample inside the pore. Therefore, a limited number of them are migrating inside the pores under the 10 mM NaCl concentration gradient. The scaled maximum positions displayed in Fig 4.7 for 2 nm pore particles are almost the same as non-porous particles under the effect of 10 mM NaCl.

The diffusiophoretic motion of charged porous silica particles under the concentration gradient of NaOH (10 mM) is shown in Fig 4.8. As NaOH is a strong base, it changes the pH inside the pores and a pH gradient is created along the pore in addition to the electrolyte gradient. The pH gradient can change the surface charge of silica particles significantly. As shown in Fig 4.8, both samples of porous particles do not enter inside the pores of the channel, and they are creating a small depletion zone over the entrance of the pores. This means a diffusiophoretic velocity in the negative x-direction is imposed on them which is in the opposite direction of the case of the non-porous particle.

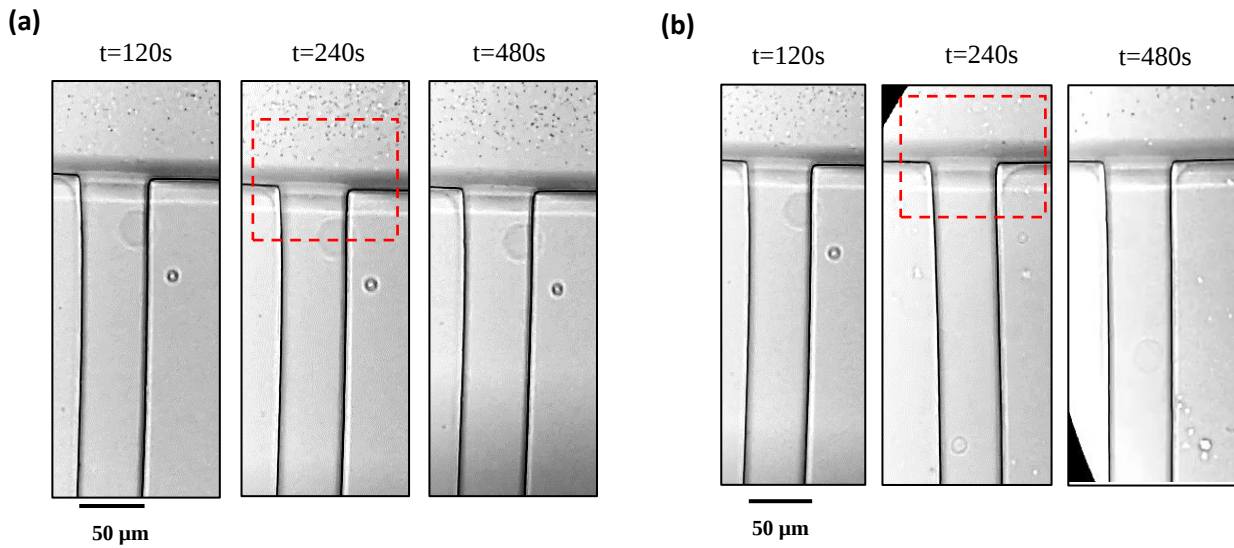


Fig 4.8 Diffusiophoretic motion of porous silica particles under the concentration gradient of 10mM NaOH. (a) Time sequence images for 1 μm porous silica particles with 2 nm pore size. (b) Time sequence images for 1 μm porous silica particles with 10 nm pore size.

All conditions for non-porous and porous particles in the case of 10 mM NaOH are the same; however, non-porous particles migrate inward the channel pores and porous particles migrate outward the channel pores, forming a small exclusion zone of particles over the pores. The only parameter that can be different is the sign of the effective surface charge of porous particles compared to non-porous particles in the presence of NaOH electrolytes. Also, a similar behavior for porous particles has been observed in a 5 mM NaOH solution.

The zeta potential measurements of porous particles in DI water and 10 mM NaOH solution are shown in Table 4.1. The porous particles' zeta potential in 10 mM NaOH is similar to the zeta potential of porous particles in DI water, while for the non-porous particles, a significant difference in zeta potential is observed in the electrolyte solution.

Table 4.1 Zeta potential measurements of non-porous and porous particles with DLS instrument in DI water and 10 mM NaOH solution.

Particle sample	Zeta potential in DI water	Zeta potential in 10 mM NaOH
Porous silica with 2nm pores	-35.62 ± 0.94 mV	-41.72 ± 3.53 mV
Porous silica with 10nm pores	-42.2 ± 0.45 mV	-42.7 ± 1.77 mV
Non-porous silica	-51.73 ± 0.71 mV	-98.43 ± 4.89 mV

The zeta potential is the electric potential at the location of the slipping plane in the electric double layer but the diffusiophoretic mobility for porous particles is a function of the surface charge of porous particles, which can be significantly different from each other. In the high pH created by 10 mM NaOH, we hypothesize counterions (positive ions) are attracted to the surface of porous particles (the interior region and outer region) and make a temporary positive surface charge for porous particles. Therefore, porous particles' effective surface charge is positive temporarily resulting in migration in the negative x-direction and creating a temporary small depletion zone near the entrance of the pores[139]. After the concentration gradient of NaOH disappears (~300s), the only imposed velocity on porous particles is the convective velocity in the y-direction and the surface charge of particles will become negative again. Therefore, the generated small depletion zone disappears by the Brownian motion of particles in the y-direction as mentioned in chapter 3.

4.4 Conclusions

Porous particles can be used in various applications such as separation and drug delivery where a concentration gradient of ions can be present or be developed as desired in such systems. Among several factors that can influence the mobility of porous particles, we highlighted the influence of

pore size on the permeability, and the electrolyte concentration gradient in the range of a thin double layer.

We investigated the diffusiophoretic motion of non-porous and porous silica particles in a dead-end pore channel in two different electrolytes experimentally. The porous silica particles show a lower drag force up to 65% compared to the non-porous silica particles in the solution using an optical tweezers instrument to measure the drag force. The pore size of porous particles has a significant influence on the overall drag force of particles. Although the particles with 2 nm pores in our experiments have a larger surface area compared to particles with a pore size of 100 nm, the measured drag force for the particles with larger pores was 50% lower than that of particles with smaller pores.

Also, we observe that sodium hydroxide salt leads to faster diffusiophoretic motion in comparison with sodium chloride for non-porous silica particles due to the higher zeta potential of particles in NaOH and higher β than NaCl. These two parameters are playing a main role in the diffusiophoretic mobility of non-porous particles as shown in eq (4.2). On the other hand, the diffusiophoretic mobility of porous particles is more complex than non-porous particles. The surface charge density, β , κa , and surface area affect the diffusiophoretic mobility of porous particles. Under the concentration gradient of NaCl and NaOH, the chemiphoretic contribution reduces to zero due to the high value of κa . Therefore, the electrophoretic contribution is the only source for creating diffusiophoretic mobility and the particle motion is dictated by the net local electric field and the effective zeta potential of the porous particles.

In the 10 mM NaCl, the small value of surface charge density and the reduced hydrodynamic drag force play crucial roles in the diffusiophoretic motion of porous particles in dead-end pore geometries. Both of these parameters prevent porous particles to move inside the pore along the concentration gradient and significantly alter the behavior of particles depending on the pore size. For particles with large pores, this effectively diminishes any diffusiophoretic movement into the dead-end channels, while particles with smaller pores are still driven into the channels. This implies that when working with porous particles in electrolyte solutions, the interaction between the electrolyte and the particle pores will dictate effective transport. When changing the salt to 10 mM NaOH, the effective surface charge of porous particles temporarily changes to a positive surface charge causing the push away of the porous particles from the entrance of the pores,

forming an exclusion zone similar to the observations in Chapter 3. This behavior under the effect of 10 mM NaOH can be utilized in the micro-scale manipulation of particles.

Our work shows that the interaction of the porous particles, the pore size, and the background electrolyte have a large influence on the diffusiophoretic behavior of porous particles, indicating that for applications the system should be studied to sufficient detail before implementation.

Chapter 5

5 Conclusions and Recommendations

In this dissertation, the phoretic motion of non-porous and porous colloidal particles under the effect of a solute concentration gradient was investigated experimentally in a dead-end pore microfluidic channel. First, the influence of PDMS interaction with available ions in DI water on the particles' motion was studied without introducing any background concentration gradient. In this part, the effect of particle size, the injection flow rate, and different sizes for the width of the pores was explored over time. Next, the phoretic motion of non-porous and porous particles under an imposed electrolyte concentration gradient was studied. The previous studies explained the porous particles' motion under the effect of concentration gradient numerically. In this work, the diffusiophoretic behavior of porous particles was compared to non-porous particles experimentally based on the drag force measurements, the influence of surface charge density, and the porosity of porous particles as a function of pore size.

The first novel aspect of this work is to study the influence of the PDMS wall interfacial interaction with present ions in DI water without introducing any background concentration gradient in the channel. We showed the interfacial chemistry of the microfluidic platform can have a significant influence on the particles' movement and the impact of this interfacial chemistry needs to be considered in lab-on-a-chip designs. A second novel contribution is the investigation of the diffusiophoretic motion of porous particles experimentally and the comparison with the case of non-porous particles. Based on our knowledge, the migration of porous particles under the effect of an imposed concentration gradient has not been investigated experimentally in previous studies. The interior microstructure of colloidal particles can significantly change the particles' diffusiophoretic behavior. Therefore, it is crucial to study the diffusiophoretic motion of porous particles and distinguish it from the case of non-porous particles.

5.1 Conclusions

First, the effect of PDMS interaction with available ions present in DI water inside the channels was found can create a transient diffusiophoretic motion in colloidal particles (chapter 3). We have

shown that in dead-end pore geometry without introducing any electrolyte into the channel a temporary spontaneous concentration gradient between the pores and the main channel would be created due to the interaction of the PDMS wall inside the pores with ions in DI water ($\text{H}^+, \text{HCO}_3^-$). This indicates that even without using ion exchange membranes and a background concentration of electrolyte, as conventionally done[31], [51], [119], we can create an exclusion zone in the channel. This self-generated concentration gradient results in the accumulation of colloidal particles in the main channel and pushes them away from the pores of the channel to create a particle-free zone in the main channel which is called an exclusion zone. The exclusion zone development in our system without introducing any background electrolyte has a significant role in the PDMS dead-end pore microfluidic channel. This effect needs to be considered at the initial stage of the experiments because it can affect the migration of colloidal particles in the channel.

We found the thickness of the generated exclusion zone depends on the Sherwood number which is the ratio of the longitudinal convective transfer to the transverse diffusion rate. As Sh increases, the thickness of the exclusion zone decreases because the convective velocity increases, and the balance of velocities on particles at the entrance of the pores will be dominated by the convective velocity. Also, it was found that the width of the pores does not affect the exclusion zone establishment as the density of available ions remains constant as the pore width changes. Furthermore, we have investigated the effect of particle size on the exclusion zone generation. The results for two different sizes of colloidal particles showed that the size does not change the thickness of the exclusion zone; whereas, it will affect the temporal stability of the exclusion zone. The diffusion coefficient of colloidal particles depends on the particle size based on the Stokes-Einstein equation. The influence of the diffusiophoretic velocity on the colloidal particles reduces over time as the concentration gradient is decreasing. Therefore, the migration of the particles in the transverse direction is getting increasingly dominated by the Brownian motion over time. This means the exclusion zone disappears in a shorter time for the smaller particles compared to larger particles because their diffusion coefficient is larger.

In chapter 4, the diffusiophoretic motion of porous particles under the influence of electrolyte concentration gradient was explored and compared with non-porous particles. We investigated the effect of pore size, electrolyte concentration gradient in the range of a thin double layer, and the relative difference in diffusivity of ions (β). It should be mentioned that the effect of the interaction

of PDMS with DI water on the particles' motion can be neglected when there is a concentration gradient of electrolyte in the system because the influence of the concentration gradient of the introduced electrolyte would be dominant due to the electrophoretic contribution which is significantly higher than the chemiphoresis effect[41]. In the case of the non-electrolyte concentration gradient, the effect of the PDMS interaction with the solution should be considered because the phoretic motion of particles in the non-electrolyte concentration gradient is caused by the chemiphoresis, but the interaction of PDMS with the solution is creating the electrophoretic contribution as well.

At first, we showed the measured drag force for porous particles is up to 65% smaller than non-porous particles based on the pore size. As the pore size decreases, the measured drag force for porous particles increases and gets closer to the non-porous particles' drag force. We then studied the diffusiophoretic motion of porous and non-porous silica particles in a dead-end pore microfluidic channel. For non-porous particles, we observed the diffusiophoretic motion of particles in the NaOH concentration gradient is higher than the NaCl concentration gradient due to the higher magnitude of zeta potential of silica particles in NaOH solution and higher β compared to NaCl.

For porous particles, various parameters play a role in the diffusiophoretic motion such as surface charge density, β , κa , pore size and surface area which both can affect the permeability based on the interconnectivity of pores. One of the most important differences between porous particles and non-porous particles is the effect of surface charge density. For porous particles, the surface charge density affects the diffusiophoretic mobility; whereas, the zeta potential is the parameter controlling the diffusiophoretic mobility for non-porous particles. The zeta potential is the potential around the particles on the slipping plane which could be significantly different from the potential on the surface of porous particles because counterions can be attracted into the interior region of porous particles and affect the surface charge density.

In the 10mM concentration of NaCl or NaOH, the value of κa is large which makes the porous particles effectively chargeless. Therefore, the chemiphoretic contribution is zero and the diffusiophoretic motion of particles solely stems from the electrophoretic contribution[39], [41], [43]. Under the imposed concentration gradient by the 10 mM NaCl in the dead-end pore microfluidic channel, we found that the diffusiophoretic velocity compared to the convective

velocity is small due to the small surface charge density and the reduced hydrodynamic drag force. Therefore, porous particles cannot diffuse into the pores along the concentration gradient because both of the mentioned parameters are reducing the influence of diffusiophoretic velocity.

Under the concentration gradient of 10 mM NaOH, we observed the particles are being pushed away from the entrance of the pores over time and creating an exclusion zone over the pore entrance. We hypothesize the effective surface charge of porous particles changes to a positive surface charge temporarily because this could be the only reason causing the direction of particles' motion changes to the opposite direction. After the effect of 10 mM NaOH concentration disappears, the porous particles' surface charge returns to negative and particles will move back toward the entrance of the pores without being pushed away.

The observations in our experimental setup for non-porous and porous particles displayed that the diffusiophoretic motion of porous particles could be very complex due to the interactions of porous particles with the ions in the solution which can affect significantly the surface charge density of particles. Also, the pore size and the surface area of particles can affect the permeability of porous particles which is an effective factor in diffusiophoretic mobility. Therefore, the phoretic motion of porous particles with different properties should be studied in sufficient detail before implementation.

5.2 Recommendations and Future Directions

At the end of this research, based on the obtained results and insights from the experimental study on the diffusiophoretic motion of non-porous and porous particles in a PDMS microfluidic channel, recommendations for further research of this work can be made;

1. As explained in the previous section, our work shows the behavior of porous silica particles under the effect of an electrolyte concentration gradient. However, the behavior of porous particles is very complex due to the effect of various parameters such as porosity, and porous structure which can affect the permeability, and the pore sizes. Therefore, each of these parameters needs to be explored separately to have a comprehensive understanding of the influence of each of these parameters on the diffusiophoretic motion of porous particles.

2. The dead-end pore geometry provides a transient concentration gradient which means the diffusiophoretic behavior is changing over time. To simplify the situation in the experimental setup for the diffusiophoretic motion of porous particles, open pores or H-shaped microfluidic channels can be used to be able to generate a steady-state concentration gradient in the channel. In these configurations, the diffusiophoretic velocity of colloidal particles can be calculated as it is constant during each concentration gradient considering the influence of diffusioosmotic velocity. Therefore, the diffusiophoretic mobility of colloidal particles can be calculated using eq (4.1). In this way, the diffusiophoretic mobility can be calculated for porous particles in different conditions as a function of porosity, pore size, β , and surface charge density. Then, the calculated diffusiophoretic mobility based on experimental data can be compared to the numerical data shown in the previous studies.
3. One of the common porous particles used in drug delivery applications is polyelectrolytes such as DNA and proteins. The diffusiophoretic motion of polyelectrolytes requires to be explored and the differences between porous silica particles and polyelectrolytes should be distinguished as polyelectrolytes are macromolecules and have different porous structures compared to porous silica particles.
4. The presence of multiple ions in the solution is a common condition in various applications. Therefore, it is worth studying the effect of the presence of multiple ions on the diffusiophoretic behavior of colloidal particles. The diffusiophoretic motion of non-porous particles in the presence of multiple species has been explored both theoretically and experimentally[30], [80]. However, it has not been explored for porous particles theoretically or experimentally. Thus, a potential study to explore is the diffusiophoretic motion of porous particles in the presence of multiple species both numerically and experimentally.

Appendix A

Supplementary information for chapter 3

A 1. Exclusion zone establishment over time.

Further pictures of exclusion zone formation in the experiment are shown in Fig. A1. As shown in Fig. A1(b), the exclusion zone thickness along the channel length increases due to the presence of pores along the channel length.



Fig. A1 Experimental observation of the exclusion zone formation in dead-end channel for pore width = 100μm. (a) For 1 μm silica particles at t=3min over the first pore. (b) For 2 μm silica particles at t=3min over pores 4 to 6.

A 2. Obtaining ions' exclusion zone thickness using boundary layer analysis.

We considered a steady-state condition for eq 2.3 in the main text to be able to obtain a solution for the exclusion zone thickness analytically as

$$D_{Heff} \frac{\partial^2 c_H}{\partial x^2} + D_{Heff} \frac{\partial^2 c_H}{\partial y^2} - \frac{\partial}{\partial y} (c_H u_y) = 0 \quad (A1)$$

Where x and y are the Cartesian coordinates and u_y is the background flow velocity in the y -direction. We use characteristic scales to nondimensionalize the above equation, the dimensionless parameters are defined as

$$c_H^* = \frac{c_H}{c_{H0}}, \quad X = \frac{x}{w_{ch}}, \quad Y = \frac{y}{L}, \quad u_y^* = \frac{u_y}{\bar{u}}$$

Where c_{H0} is the bulk concentration in the pore, w_{ch} is the width of the main channel, L is the length of the main channel which includes pores and $\bar{u}$ is the mean flow velocity of the background flow. So, eq 2.5 becomes:

$$\frac{D_{Heff} c_{H0}}{w_{ch}^2} \frac{\partial^2 c_H^*}{\partial X^2} + \frac{D_{Heff} c_{H0}}{L^2} \frac{\partial^2 c_H^*}{\partial Y^2} - \frac{c_{H0} \bar{u}}{L} \frac{\partial}{\partial Y} (c_H^* u_y^*) = 0 \quad (A2)$$

Generally, we know that $L \gg w_{ch}$ which means the second term in eq (A2) is negligible compared to the first term. Therefore, eq (A2) can be simplified to

$$\frac{\partial^2 c_H^*}{\partial X^2} - Sh \frac{\partial}{\partial Y} (c_H^* u_y^*) = 0 \quad (A3) \quad Sh = \frac{w_{ch}^2 \bar{u}}{L D_{Heff}} \quad (A4)$$

Where Sh is the Sherwood number is the ratio of longitudinal convective transfer to the transverse diffusion rate which links most of the physicochemical parameters (flow rate, diffusivity of ions, and geometrical factors).

We propose a trial solution for the concentration profile of H^+ over the first pore as a function of exclusion zone thickness to derive an analytical solution for the exclusion thickness. For this purpose, we have defined a coordinate transform of $x = \xi - \frac{w_{ch}}{2}$ and $y = \eta$ and establish the concentration profile in this coordinate as

$$c_H = \begin{cases} c_{H\infty} + c_{H0} \frac{\delta - \xi}{\delta} & \xi < \delta \\ c_{H\infty} & \xi \geq \delta \end{cases} \quad (A5)$$

Where δ is the exclusion layer thickness as a function of η and $c_{H\infty}$ is the bulk concentration in the main channel. Then, substituting eq (A5) in eq (A3) and integrating the differential equation could result in the von Karman integral balance as

$$D_{Heff} \left. \frac{\partial c_H}{\partial \xi} \right|_{\xi=0} + \int_0^\delta u_\eta \frac{\partial c_H}{\partial \eta} d\xi = 0 \quad (A6)$$

As background flow is laminar and fully developed in the channel, the velocity profile over the first pore in the y-direction can be obtained through the Poiseuille flow equation between parallel plates with specific boundary conditions[108].

$$u_y = \frac{-\Delta p}{2\mu L} x^2 + c_1 x + c_2 \quad (A7)$$

The governing boundary conditions by considering full slip condition for the lower side and no-slip condition for the upper side are:

$$\begin{cases} (1) \text{ at } x = \frac{w_{ch}}{2} \rightarrow u_y = 0 \\ (2) \text{ at } x = -\frac{w_{ch}}{2} \rightarrow \frac{du_y}{dx} = 0 \end{cases} \quad (A8)$$

The final equation for flow velocity after calculating the coefficients by substituting the boundary conditions in eq (A7) would be as follows

$$u_y = \frac{-\Delta p}{2\mu L} x^2 - \frac{-\Delta p w_{ch}}{2\mu L} x + \frac{3\Delta p w_{ch}^2}{8\mu L} = \frac{-\Delta p w_{ch}^2}{2\mu L} \left(\left(\frac{x}{w_{ch}} \right)^2 + \frac{x}{w_{ch}} - \frac{3}{4} \right) \quad (A9)$$

Eq (A9) after substituting the coordinate transform ($x = \xi - \frac{w_{ch}}{2}$) would be simplified to

$$u_y = \frac{3}{2} \bar{u}_y \left(\frac{5}{4} - \frac{\xi}{w_{ch}} - \left(\frac{\xi}{w_{ch}} - \frac{1}{2} \right)^2 \right) = \frac{3}{2} \bar{u}_y \left(1 - \left(\frac{\xi}{w_{ch}} \right)^2 \right) \quad (A10)$$

Substituting the flow velocity equation in eq (A6) and calculating the integral would be as follows if assume $\delta \ll 2w_{ch}$

$$\int_0^\delta u_\eta \frac{\partial c_H}{\partial \eta} d\xi = \int_0^\delta \frac{3}{2} \bar{u}_y \left(1 - \left(\frac{\xi}{w_{ch}} \right)^2 \right) \frac{c_{H0}}{\delta^2} \frac{d\delta}{dy} \xi d\xi = \frac{3}{4} \bar{u}_y c_{H0} \frac{d\delta}{dy} \left(1 - \frac{\delta^2}{2w_{ch}^2} \right) \quad (A11)$$

$$-D_{Heff} \frac{c_{H0}}{\delta} + \frac{3}{4} \bar{u}_y c_{H0} \left(1 - \frac{\delta^2}{2w_{ch}^2} \right) \frac{d\delta}{dy} = 0 \quad (A12)$$

$$\delta^2 = \frac{8 D_{Heff}}{3 \bar{u}_y} y \quad (A13)$$

A 3. Obtaining particles' exclusion zone thickness using particles' trajectory analysis.

The particles' exclusion thickness can be obtained based on the particles' trajectory in the main channel. The fluid flow in the channel is considered to be laminar ($Re \sim 0$) and the sedimentation effect is neglected. The particles' streamline on the exclusion zone boundary layer is as follows

$$\frac{dx}{dt} = \frac{d\xi}{dt} = U_{DP} \quad (A14)$$

$$\frac{dy}{dt} = u_{y,max} \quad (A15)$$

$u_{y,max}$ is the maximum velocity of the flow rate in the y-direction. The colloidal particles close to pores are migrating away from the pores of the channel where the flow has a no-slip boundary condition in the y-direction. The diffusiophoretic velocity equation based on the hydrogen concentration profile leads to

$$U_{DP} = D_{DP} \nabla \ln C = -\frac{D_{DP}}{C_H} \frac{C_{H0}}{\delta} = -D_{DP} \frac{C_{H0}}{\delta C_{H\infty} + c_{H0}(\delta - \xi)} \quad (A16)$$

At the particles' streamline ($\xi = \delta_p$), eq (A16) can be simplified to

$$U_{DP} = D_{DP} \nabla \ln C = -\frac{D_{DP}}{C_{H\infty}} \frac{C_{H0}}{\delta} \quad (A17)$$

Dividing eq (A14) to eq (A15) and considering eq (A17) at the particles streamline boundary,

$$\frac{d\delta_p}{dy} = \frac{\frac{D_{DP}}{C_{H\infty}} \frac{C_{H0}}{\sqrt{\frac{8}{3} \frac{D_{Heff}}{\bar{u}_y} y}}}{\frac{3}{2} \bar{u}_y} \quad (S18)$$

Eq (3.11) in the main text shows that the particle exclusion thickness is a function of the inverse square root of flow velocity ($\sqrt{\frac{1}{u_y}}$). As shown in Fig. A2, the ratio of normalized particles'

exclusion thickness in two different flow rates is representing the same results in the experimental data and theoretical calculation.

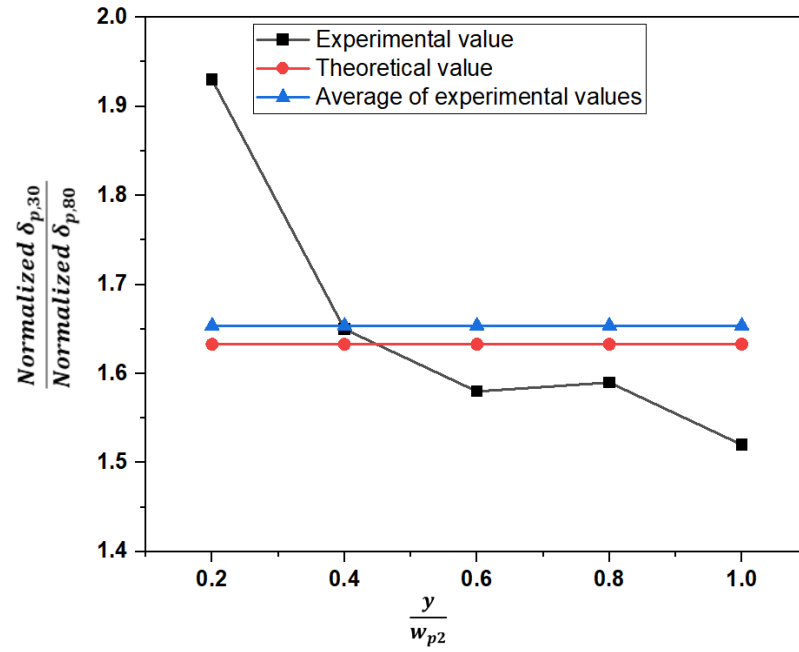


Fig. A2 The ratio of normalized particle exclusion thickness in two flow rates. The black curve shows the experimental value in each position. The blue and red lines display the average values over the first pore in experiment and theory, respectively.

A 4. Exclusion zone development in the main channel for different flow rates

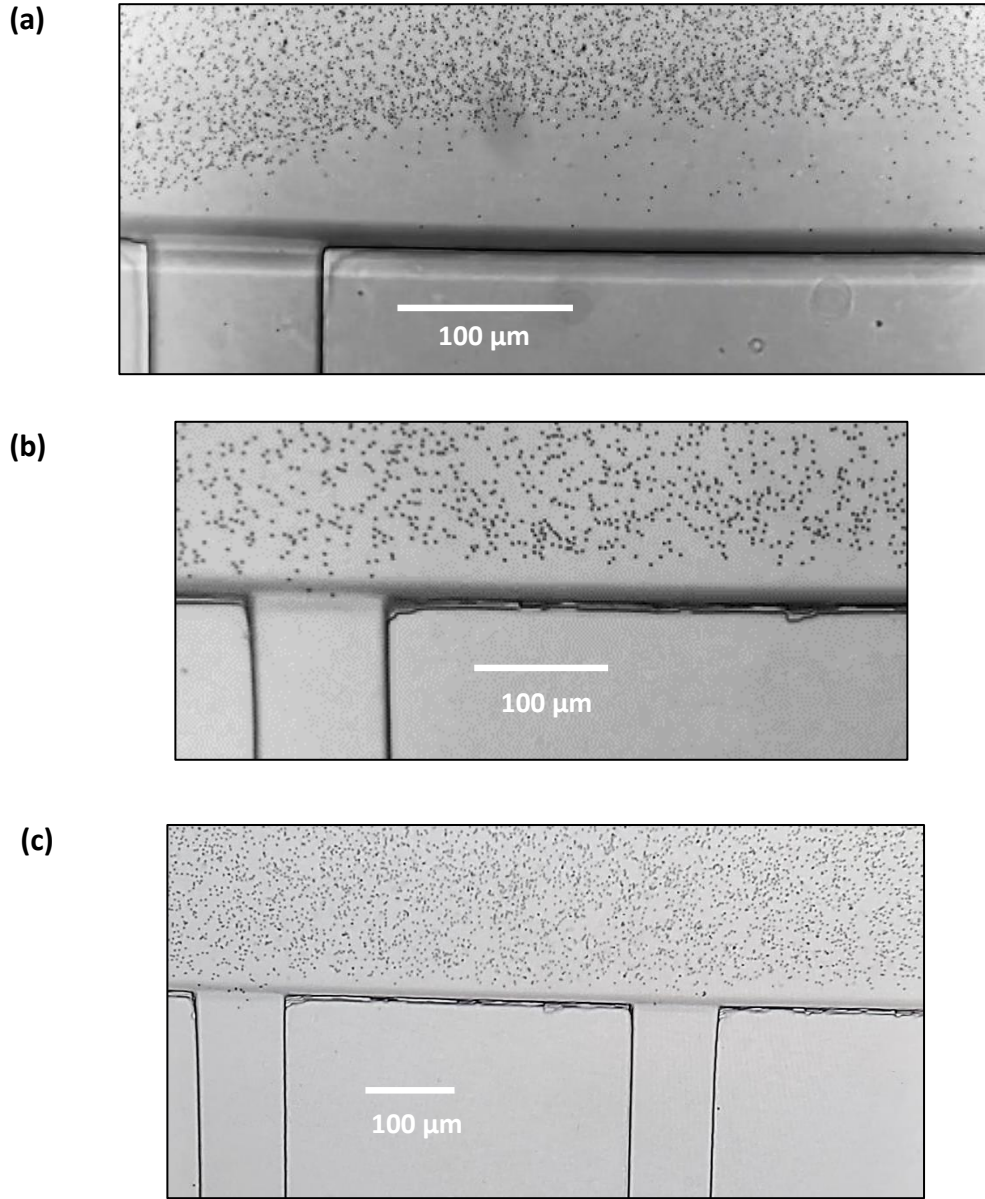


Fig. A3 The maximum exclusion zone in the main channel for 100 μm pore width. a) the exclusion zone development for flow rate 30 $\mu\text{L/h}$. b) the exclusion zone development for flow rate 55 $\mu\text{L/h}$. c) the exclusion zone development for flow rate 80 $\mu\text{L/h}$.

As shown in Fig. A3, when the flow rate in the main channel increases, the exclusion zone thickness decreases confirming the effect of Sh described in the theoretical part.

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