PHENOMENA AFFECTING THE RATE AND EQUILIBRIUM OF AQUEOUS CHEMICAL REACTIONS IN NANOCHANNELS

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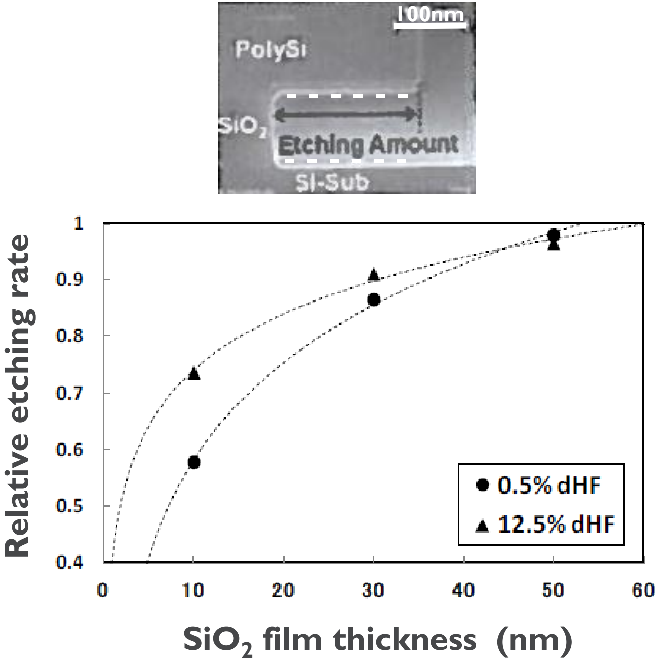
INTRODUCTION

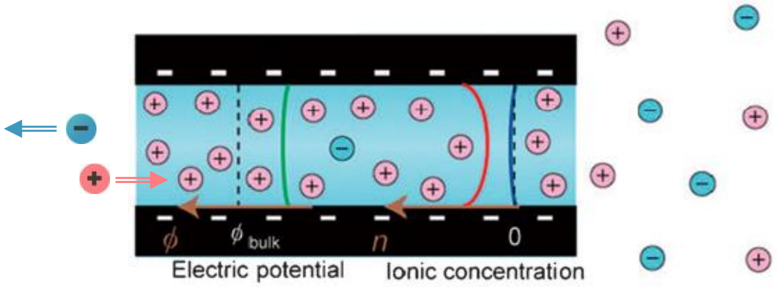
HF ETCHING OF SIO_2 IN FILLED NANOCHANNELS

KINETICS AFFECTED BY OVERLAP OF ELECTROSTATIC DOUBLE LAYERS (EDL)



→ Decreased etch rate in narrow channels

- EDL overlap in nanochannel



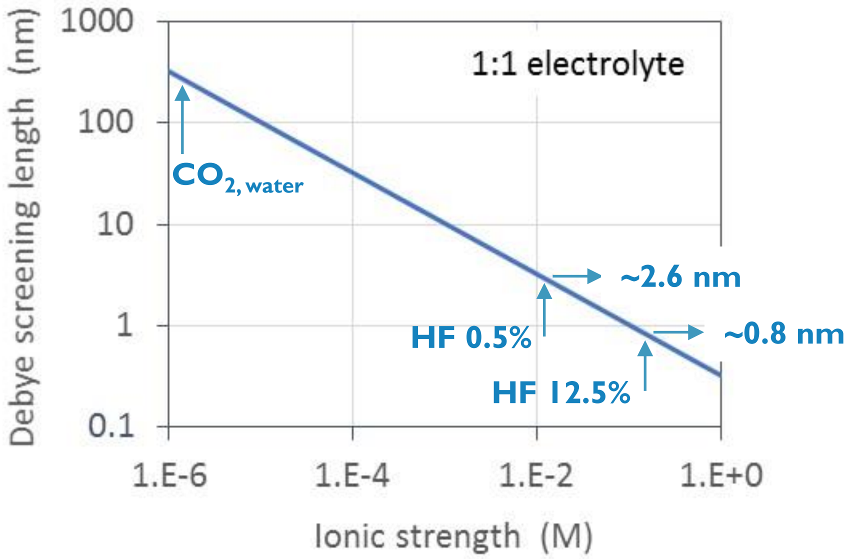
H. Daiguji, *Chem. Soc. Rev.*, 2010, **39**, 901.

- No electroneutral 'bulk' solution
  - Depletion of ions with same charge as surface; enrichment of …
  - → Acidic pH shift
  - → Decreasing etch rate from increasing depletion of HF_2^-

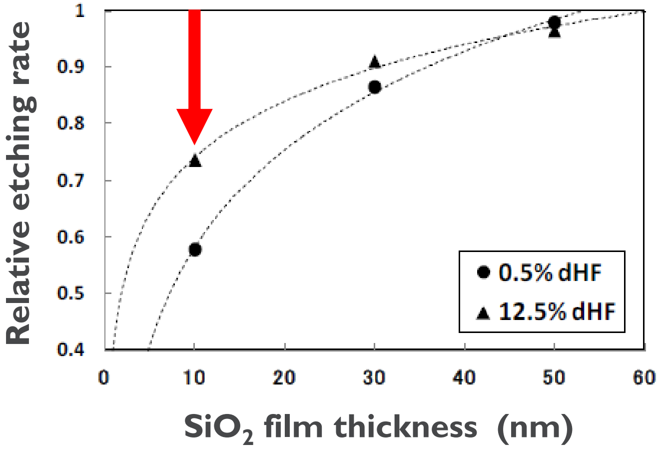
HF ETCHING OF SIO_2 IN FILLED NANOCHANNELS

EVALUATION OF IMPACT OF EDL OVERLAP

- EDL thickness in HF solutions



→ No EDL overlap in HF 12.5 %



- Etch rate decrease in HF 12.5 % cannot be explained by EDL overlap

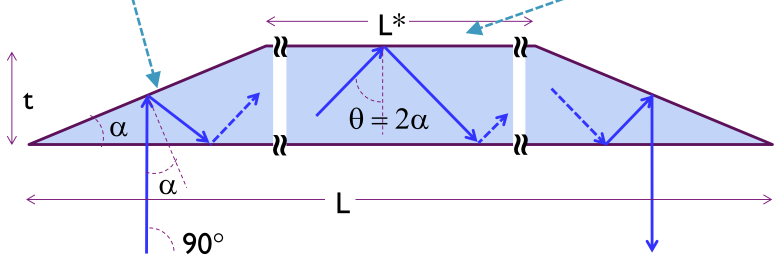
→ What else ?

THIS WORK

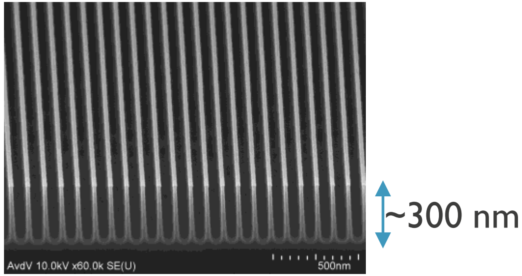
PROBING THE CHEMISTRY IN NANO-SPACES USING ATR-FTIR

ATR CRYSTAL MADE FROM SI WAFER WITH NANO-STRUCTURES[1,2]

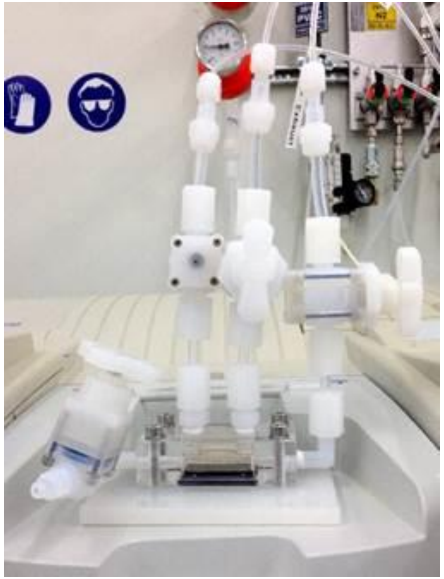
Total reflection → α > 17.1° (Si/air)
→ TR at top surface



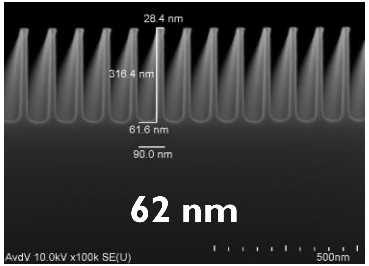
Top surface covered with nanochannels

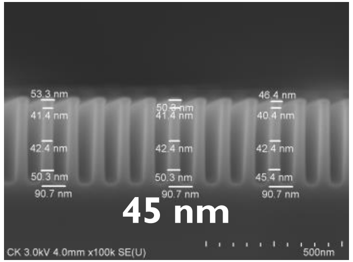


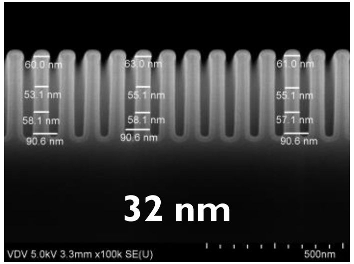
Liquid cell on top of ATR crystal

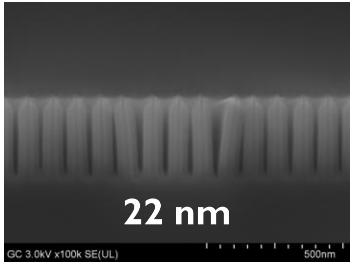


Channel width decreased by SiO_2 deposition (PE-ALD)









[1]G. Vereecke et al., *ECS J. Solid State Sci. Technol.* **3** (2014) N3095-N3100. [2]N. Vrancken et al., *Langmuir* **33** (2017) 3601−3609.

OUTLINE

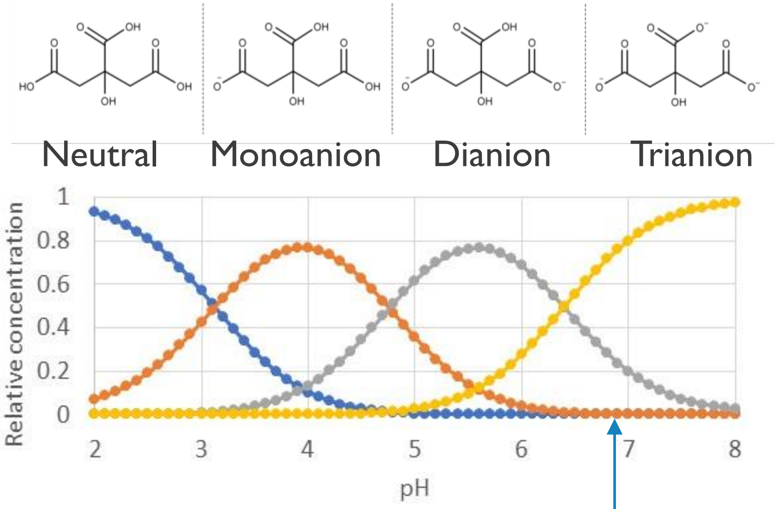
1. Measurement of pH in nanochannels
2. Impact of nano-confinement on the kinetics of a model reaction

1. MEASUREMENT OF pH IN NANOCHANNELS

INDIRECT MEASUREMENT OF pH BY FTIR

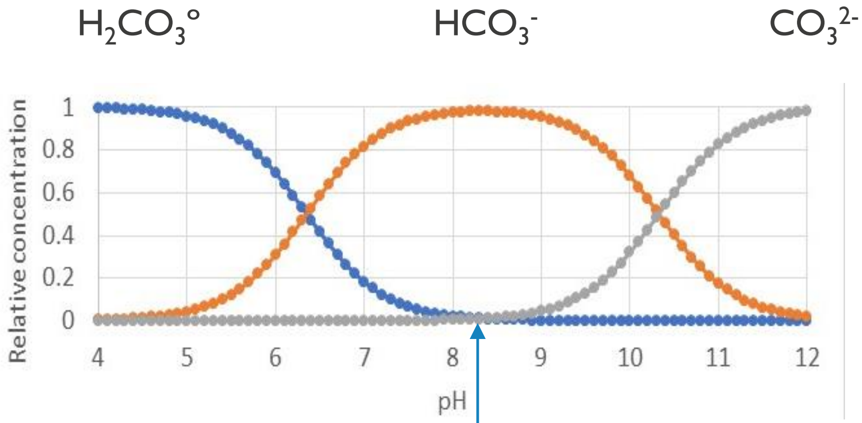
MEASURING THE PROTONATION OF ACIDIC GROUPS

- Citric acid solutions



This work:
- 50 mM citric acid (pH = 2.2)
- pH = 6.9 by NaOH addition

- Sodium bicarbonate solutions

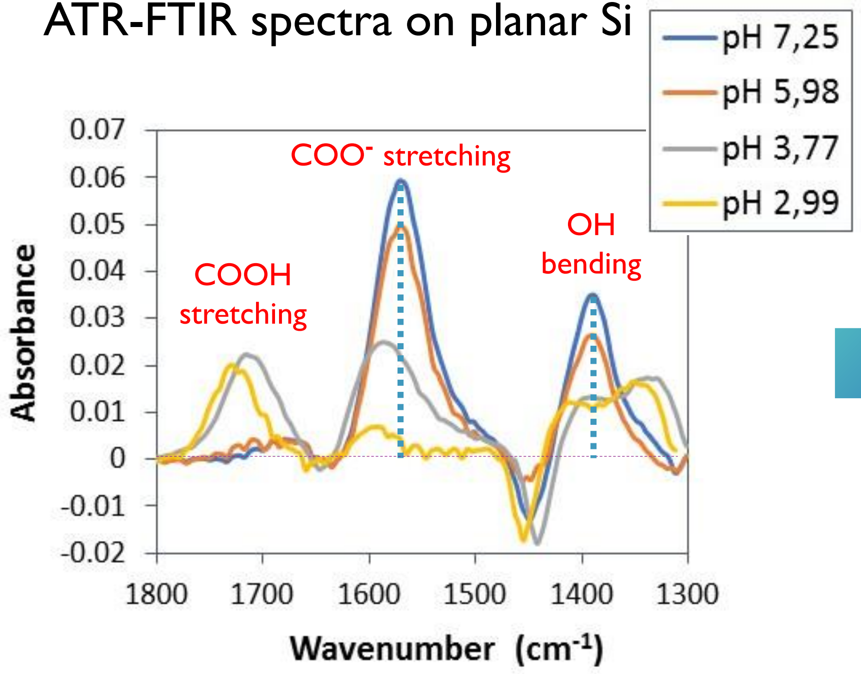


This work:
- 100 mM $NaHCO_3$ (pH = 8.3)
- In D_2O

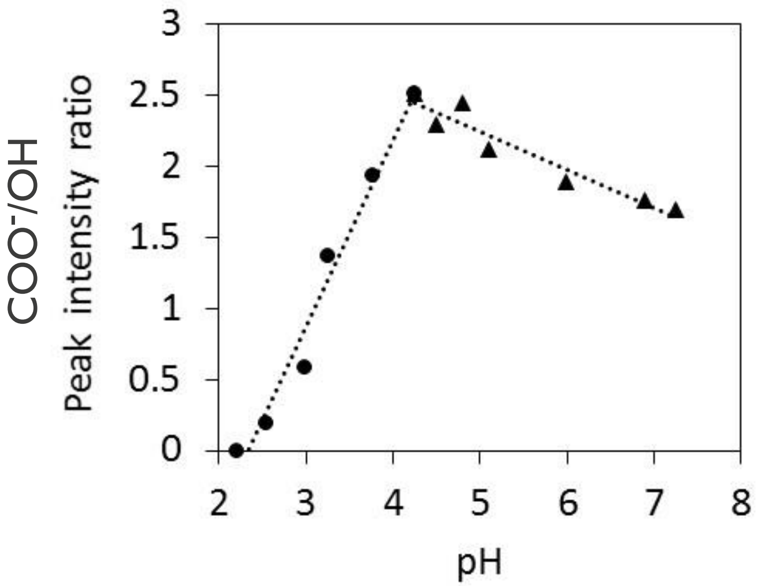
FTIR pH CALIBRATION CURVE FOR CITRIC ACID

pH SET BY HCl OR NaOH ADDITIONS

- ATR-FTIR spectra on planar Si

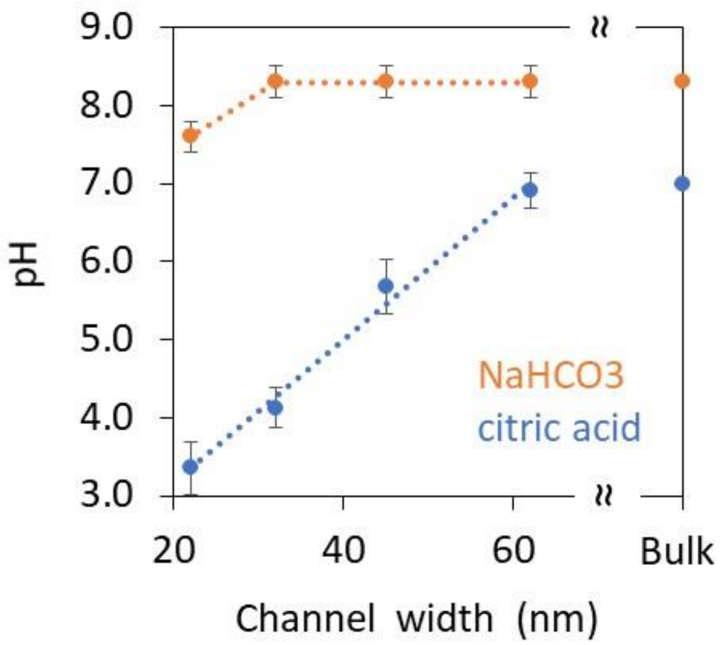


- Calibration curve



MEASURED pH IN NANOCHANNELS

DISCREPANCY BTW. MEASUREMENTS WITH CITRIC ACID AND NAHCO3



- No large $[H^+]$ variation expected at the high ionic strengths used here:

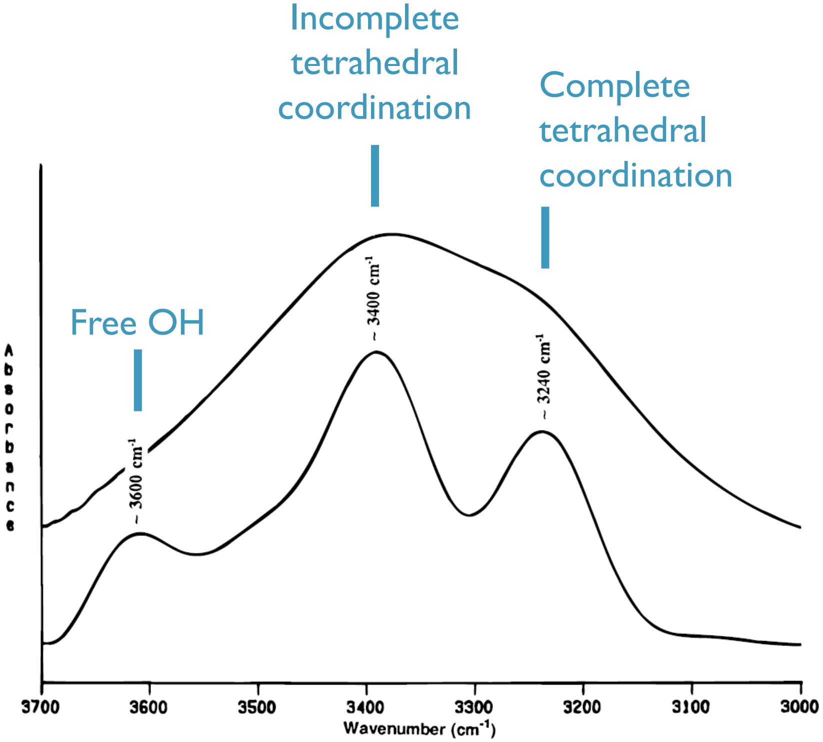
Probe molecule	Ionic strength (M)	Debye length (nm)
Citric acid	0.89	0.5
NaHCO3	0.1	1

→ No EDL overlap

- Origin of pH shift with citric acid ?

CHARACTERIZATION OF WATER H-BOND STRUCTURE BY FTIR

DECOMPOSITION OF OH STRETCHING BAND



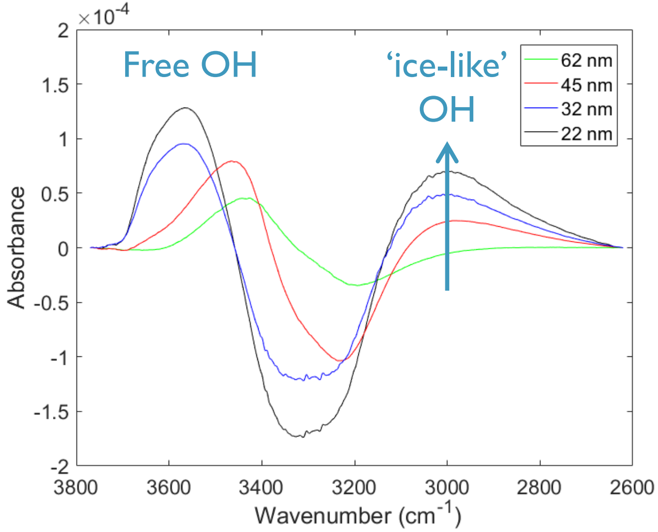
- OH stretching peak of water broadened by H-bonding
- 3 peaks obtained by Fourier self-deconvolution method[1]
  - ~3400 cm^{-1} : Hydrogen bonded water with **in**complete tetrahedral coordination
  - ~3240 cm^{-1} : Hydrogen bonded water with **complete** tetrahedral coordination, sometimes termed "ice-like"
  - ~3600 cm^{-1} : non Hydrogen-bonded or weakly H-bonded "free OH" stretch

[1]M.R. Yalamanchili et al., *Langmuir*, 1996, **12**, 4176.

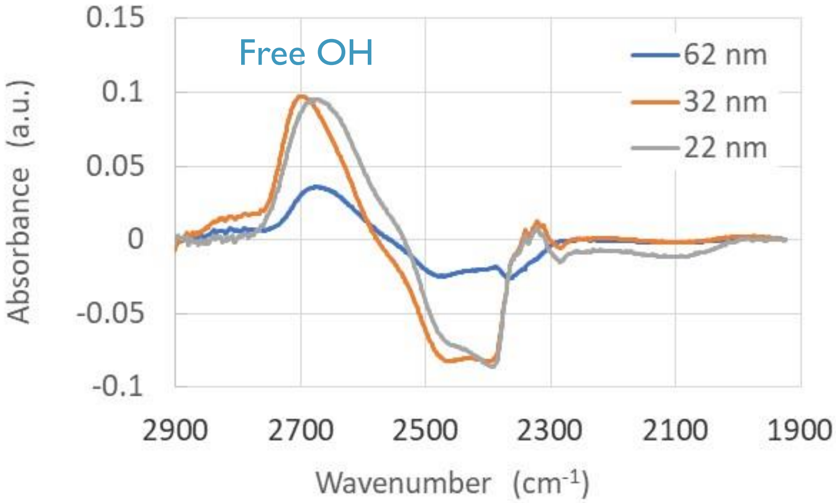
WATER STRUCTURING IN NANOCHANNELS

DIFFERENCE SPECTRA NANOCHANNEL – PLANAR SAMPLE

- Citric acid solutions



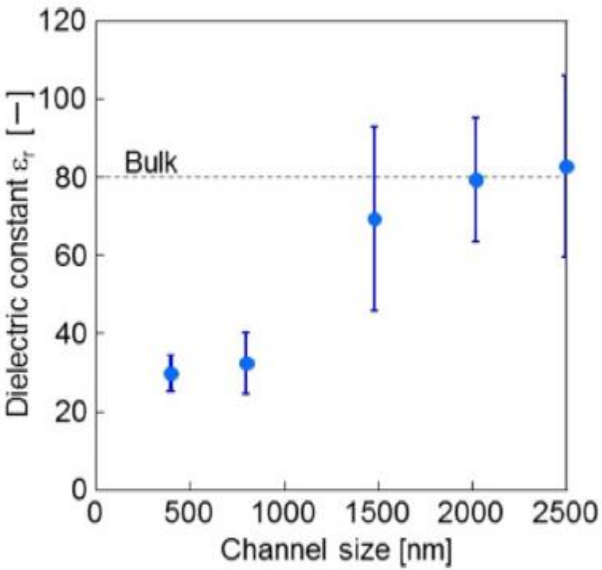
- Sodium bicarbonate solutions



- Good correlation btw. formation of 'ice-like' water and pH shift

POSSIBLE EXPLANATION FOR pH SHIFT IN NANOCHANNELS

- Lower dielectric constant of aqueous solutions in nanochannels from water structuring[1]



H_2O behaving as a solvent with lower polarity

→ Decreased screening of ions from acid dissociation

→ Increase of the acid pK_a's

→ Depressed ionization of citric acid

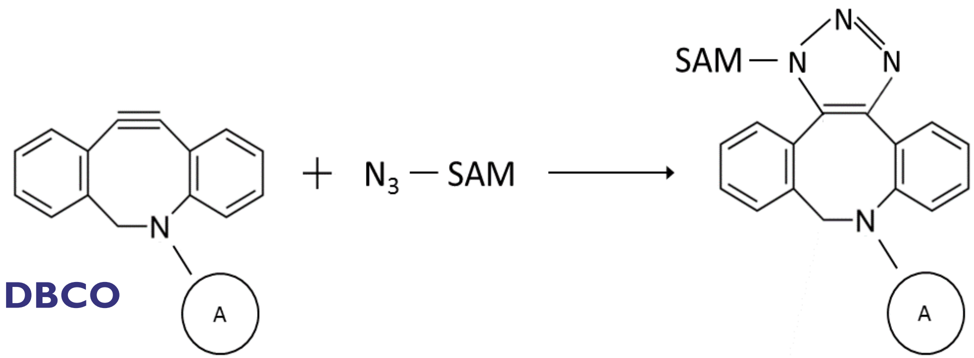
→ Shifted equilibrium, but no real pH shift

[1] K. Morikawa et al., *Anal. Chem.*, 2015, **87**, 1475.

2. IMPACT OF NANO-CONFINEMENT ON THE KINETICS OF A MODEL REACTION

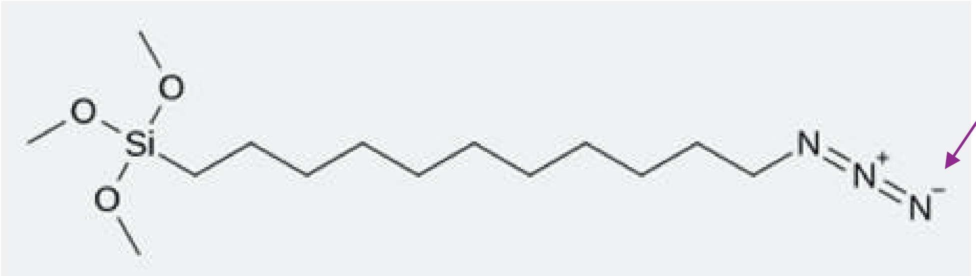
MODEL REACTION

STRAIN PROMOTED ALKYNE - AZIDE CYCLOADDITION (SPAAC)



A = PEG_3-OH

- Click Reaction
- Used in bio-sensor applications to link DNA strands to surfaces
- 2nd order reaction kinetics w/o side reactions

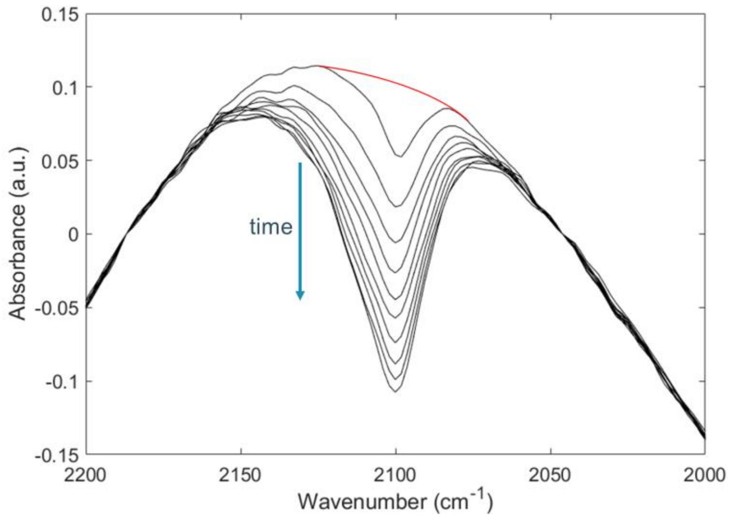


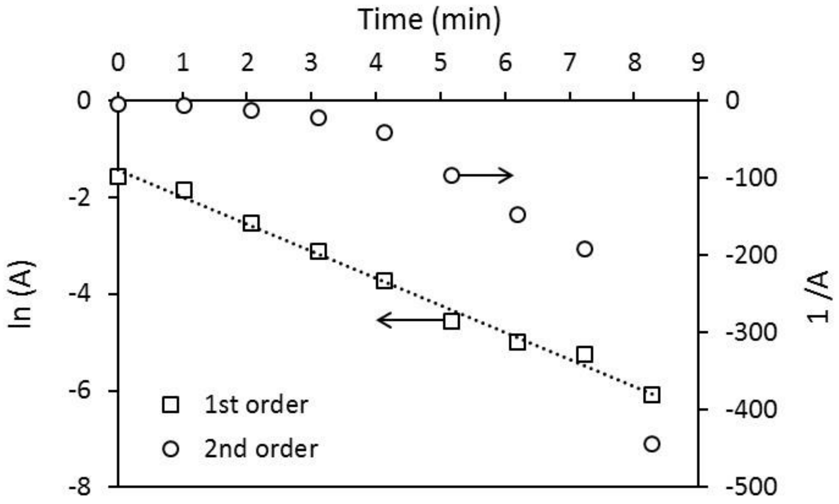
Negative surface charge

- DBCO = dibenzyl-cyclo-octyl
- PEG = poly-ethylene-glycol

KINETIC STUDY
DETERMINATION OF ORDER IN AZIDE CONCENTRATION

- Monitoring the disappearance of the azide peak at 2100 cm^{-1}





→ Pseudo first order confirmed

SLOWER KINETICS IN NANOCHANNELS VS. PLANAR

2ND ORDER REACTION CONSTANTS

Pattern	k_2 (M^{-1} s^{-1})*	k_{planar} / $k_{channel}$
Planar crystal	285 ± 27	1
64 nm channel	66 ± 2	4.3 ± 0.4
45 nm channel	54 ± 1	5.3 ± 0.5
32 nm channel	41 ± 0.5	7.0 ± 0.7

* $k_2 = \frac{k\prime}{[DBCO]_0}$; average values from 2-3 tests

- Lower reaction rates in nanochannels, decreasing along with the channel width
- EDL overlap in all conditions

Ionic strength (M)*	Debye length (nm)
2.2E-6	288

*water saturated with CO_2 gas

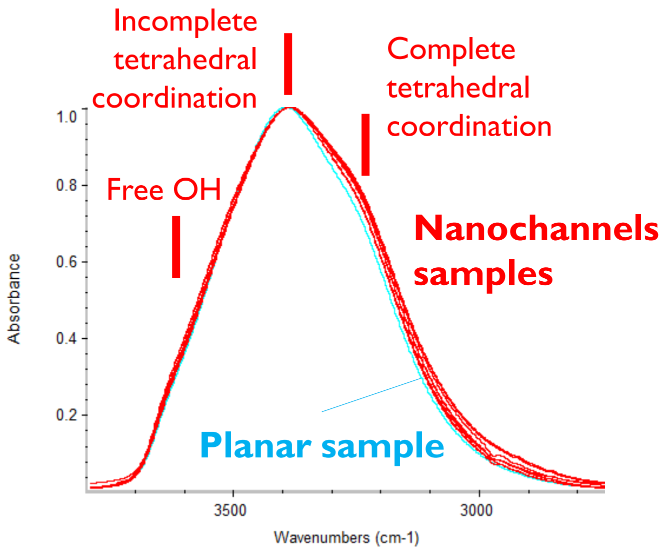
→ Nearly constant negative potential in channels in all conditions

→ No impact on concentration of neutral reactant

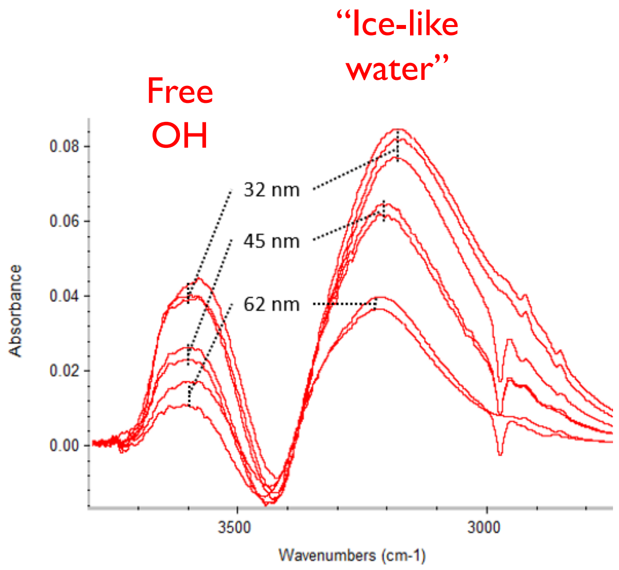
→ What else ?

WATER STRUCTURING IN NANOCHANNELS

SPECTRA FROM KINETIC TESTS



Normalized spectra after ATR correction and baseline subtraction

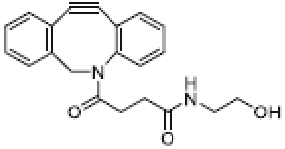
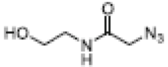
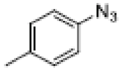
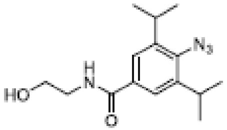
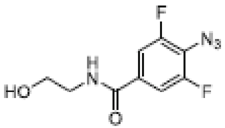


Difference spectra
Nanochannel - planar sample

- Water structuring in nanochannels, increasing as channel width decreases
- Solvent effect on SPAAC reaction ?

SOLVENT EFFECT ON SPAAC REACTIONS

REACTION RATE CONSTANTS IN DIFFERENT SOLVENT SYSTEMS[1]

Entry	Azide structure			
		ε = 69	33	15
1		1.9	0.42	0.36
2		0.90	0.33	0.21[a]
3		0.82	0.29	0.20[a]
4		0.11	0.11	0.08
5		~4[b,c]	2.3	0.77[a]
6		0.95	0.18	0.11[a]

- Solvents used in study:

Solvent system	ε^+
$D_2O:CD_3CN$ (3:1)	69
MeOD	33
H_2O:THF (1:9)	15

$^+$ calculated using eq.(3) in Wang (2001)

- SPAAC proceeds faster in more polar aqueous solvent systems

→ reaction rate decrease in nanochannels likely from water structuring

[1]J. Dommerholt et al., *Top. Curr. Chem.*, 2016, **374**, 16.

SUMMARY

SUMMARY

- Not all results obtained in this study could be explained by EDL overlap
  - pH shift measured using citric acid
  - SPAAC reaction rate decrease
- Proposed explanation: decrease of H_2O permittivity by H_2O structuring
  - Citric acid dissociation depressed, no real pH shift
  - SPAAC reaction slowed down in less polar solvent
- Water in nanochannels may behave as a solvent of lower polarity, depending on dissolved species – molecules & ions

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