Development and Application of Condense Phase Cavity Ring Down Spectroscopy

Hsiu-Fang Fan, lossie, King-chen Lin*

National Taiwan University

INTRODUCTION

There are many theoretical and experimental studies done to inspect the physical and chemical properties of silica surface. The main properties of silica surface are adjusted by the silanol group (SiOH). The average surface density of silanol groups on the surface is ~4.9 nm^{-2} , which corresponds to an average surface area of 20.4$Å^2$ per silanol group. In chromatography, the ionization degree of silanol group plays a great role for separation efficiency. From some other reports, these results pointed out that there are at least two types of silanol groups on the silica surface which contacts with water, with different pKa and different population. One has pKa=4.9 with 19% in surface population and another one has pKa=8.5 with 81% in surface population. A study done by Dong, Pappu, and Xu using crystal violet to probe the local density distribution of isolated silanol groups on silica surface had pointed out that the isolated silanol groups are surrounded by a large empty surface area (≧120 $Å^2$) and the surface density of this type is about 1.1´10^{13} cm^{-2}. In this experiment, the silanol group properties has been studied by evanescent wave cavity ring down spectroscopy in which the adsorption process in CH_3CN/ Fused silica interface.

Basic equations

1. Empty Cavity

$$I(t)=I_0 \exp\left[-(1-R)\frac{tc}{L}\right]$$

$$\tau_0=\frac{t_r}{2(1-R)}$$ **(Ring down time constant)**

***R*：Reflectivity of mirror**
***c*：Speed of velocity**
***L*：Length od cavity**
t_r = 2L/c Round-trip time

2. Analyst Presence

$$I(t)=I_0 \exp\left[-(1-R+\alpha L)\frac{tc}{L}\right]$$

$$\tau_1=\frac{t_r}{2(1-R+\alpha L)}$$

3. Absorbance

$$A=\sigma N l_s=\alpha l_s=\frac{L}{c}\left(\frac{1}{\tau_1}-\frac{1}{\tau_0}\right)$$

∗ Langmuir adsorption model :

$$\theta=\frac{N}{N_0}=\frac{KC}{1+KC}$$

$$N=N_0\bullet\frac{KC}{1+KC}$$

$$\frac{1}{\theta}=\frac{1+KC}{KC}=1+\frac{1}{KC}$$

***N*: surface density, N_0: saturation surface density**
***K*: equilibrium constant**
C : bulk concentration of sample

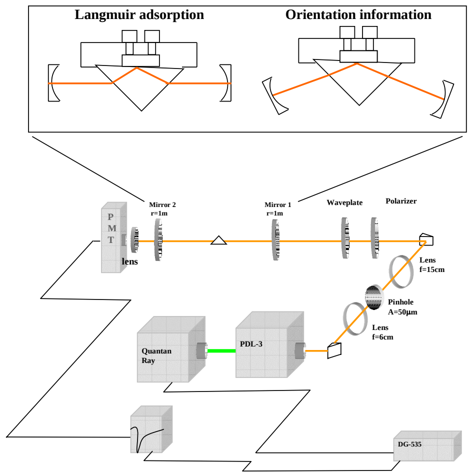
*** Orientation Information:**

$$A_p \propto a\pi\mu^2\left[\langle\cos^2\theta\rangle E_z^2+\frac{1}{2}\left(2-\langle\cos^2\theta\rangle\right)E_x^2\right]$$

$$A_s \propto \frac{a\pi\mu^2}{2}\left[\left(2-\langle\cos^2\theta\rangle\right)E_y^2\right]$$

$$\langle\cos^2\theta\rangle=\frac{2A_pE_y^2-2A_sE_x^2}{2A_sE_z^2-A_sE_x^2+A_pE_y^2}$$

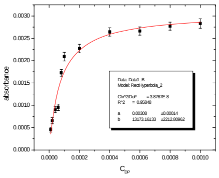
EXPERIMENT

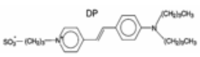


RESULTS AND DISCUSSION

I. Langmuir Adsorption:

DP (trans-4-[4-(dibutylamino)styryl]-1-methylpridiniumiodide)

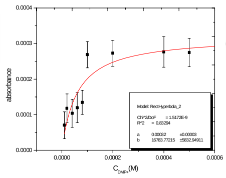


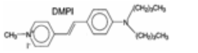


$$(SiOH)_s + (DP)_l \overset{K_{DP}}{\leftrightarrow} (SiOH\cdots DP)_s$$

K = 16666 ±810 M^{-1}
Δ***G*** = -24.2 ±1.2 kJ/mol

DMPI (trans-4-[4-(dibutylamino)styryl]-(3-sulfopropy)pyridinium)





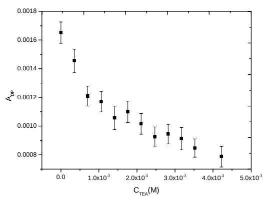
$$(SiO^-)_s + (DMP^+)_l \overset{K_{DMP^+}}{\leftrightarrow} (SiO^-DMP^+)_s$$

K = 28571 ±7150 M^{-1}
Δ***G*** = -25.6 ±6.4 kJ/mol

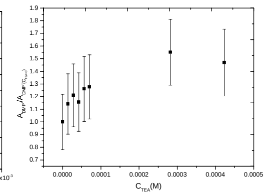
***Effect of triethylamine*:**

$$(SiOH)_s + (TEA)_l \overset{K_{TEA}}{\leftrightarrow} (SiOH\cdots TEA)_s$$

$$(SiOH\cdots TEA)_s \overset{K_{TEAH^+}}{\leftrightarrow} (SiO^-)_s + (TEAH^+)_l$$



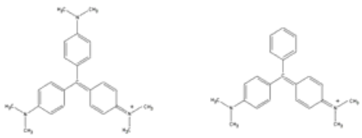
∗ The concentration of DP molecules in the solution was 0.1 mM



∗ The concentration of DMPI molecules in the solution was 0.1 mM

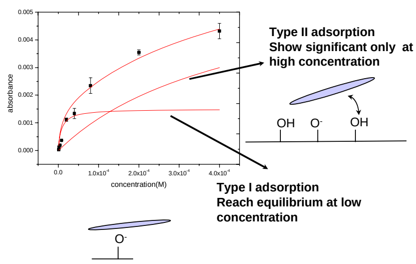
Triethylamine could abstract the protons on the surface and increase the population of SiO^-, therefore the available adsorption site for H.B. would become less so that absorbance of DP on the fused silica surface is getting small.
It is an indirect evidence that the dominant force for DP is H.B but electrostatic force for DMP^+.

II. Orientation Information:

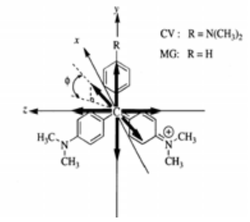


Crystal Violet **Malachite Green**

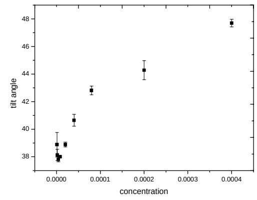
Two sites Langmuir adsorption plot for CV^+ at CH_3CN/fused silica surface:



	Type I		Type II	
	K(M^{-1})	**ΔG(kJmol^{-1})**	**K(M^{-1})**	**ΔG(kJmol^{-1})**
This Work	(1.7±0.15)×10^5	-30.1±0.2	(1.3±0.21)×10^3	-17.7±0.4
Zhi Xu et. al.[a]	1.7×10^5	-29.5	1.5×10^2	-12.3

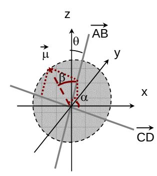


Angle Plot:



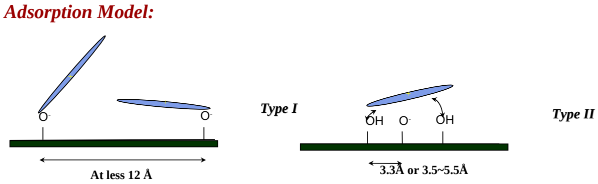
$$\langle\cos^2\theta\rangle=\frac{2A_pE_y^2-2A_sE_x^2}{2A_sE_z^2-A_sE_x^2+A_pE_y^2}$$

From literatures:
There are some experiments showed that when the surface density increases, the tilt angle for CV^+ will increase to reduce contact area between adjacent dye molecules



Literatures:
***Langmuir* 1994, 10, 3988-3993.**
***J. Colloid Interface Sci.* 1998, 198, 337-346.**

Adsorption Model:



From the Langmuir plot and angle plot , the conclusion that the adsorption for CV+ on type I silanol groupcould be more free no matter for the distance aspect and orientation aspect could be made. However, the adsorption between CV+ and type II silanol group could be more restrictedly.