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APPENDIX A

SPECTRA OF TREATED SILICA

Table A.1 Changes of IR spectra of silica by the treatment with ODS and HFD (Skoog et al., 1992)

Functional groups	Band (cm^{-1})	SiO_2 absorbance	ODS SiO_2 absorbance	HFD SiO_2 absorbance
Si-O	1000-1100	1.59	1.66	1.76
Si-OH	3300-3600	1.39	1.35	1.36
CH_2, CH_3	2850-2970	0.00	2.24	1.06
CF_2, CF_3	1200-1350	0.00	0.00	2.39

APPENDIX B

EXPERIMENTAL DATA

B.1 Data

Table B.1 Bonded ODS adsorption isotherm on silica surface

System: 180 ml of toluene, 6 g of silica with various amount of ODS

Silica	Initial concentration of ODS (μM)	Bulk phase conc. of ODS (μM)	Adsorbed ODS (μmoles/g)
ODS silica/0.3	4220.42	1045.93	95.23
ODS silica/0.5	7026.25	2706.39	129.60
ODS silica/0.7	9825.86	4136.82	170.67
ODS silica/1	14013.67	5998.60	240.45
ODS silica/2	27873.35	17065.52	324.23
ODS silica/3	41581.55	28980.23	378.04
ODS silica/4	55140.75	41999.47	394.24
ODS silica/5	68553.75	54353.06	426.01

Table B.2 Bonded HFD adsorption isotherm on silica surface

System: 100 ml of toluene, 4 g of silica, 2.5 ml of pyridine with various amount of HFD

Silica	Initial concentration of HFD (μM)	Bulk phase conc. of HFD (μM)	Adsorbed HFD (μmoles/g)
HFD silica/0.1	1849.39	893.56	23.90
HFD silica/0.5	9246.93	3847.27	134.99
HFD silica/0.7	12945.70	4492.87	211.32
HFD silica/1.0	18493.86	8694.18	244.99
HFD silica/2.0	36987.72	26481.19	262.66

Table B.3 Adsolubilization of phenol into bonded ODS

System : 15 ml of aqueous solution, 0.7 g of ODS silica (initial concentration of 183.68 ppm, pH 7)

Silica	Equilibrium Concentration (ppm)	Partitioning Coefficient, P_a	Adsolubilization constant, K_S	Adsolubilized phenol (μmoles/g)
ODS silica/0.3	166.95	0.100	22.55	3.936
ODS silica/0.5	155.95	0.178	29.41	6.523
ODS silica/1	143.88	0.277	24.66	9.362
ODS silica/2	150.62	0.220	14.51	7.778
ODS silica/3	155.26	0.183	10.38	6.685
ODS silica/4	155.70	0.180	9.77	6.580

Table B.4 Adsolubilization of phenol into bonded HFD

System : 15 ml of aqueous solution, 0.7 g of HFD silica (initial concentration of 189.47 ppm, pH 7)

Silica	Equilibrium Concentration (ppm)	Partitioning Coefficient, P_a	Adsolubilization constant, K_S	Adsolubilized phenol (μmoles/g)
HFD silica/0.1	185.15	0.023	20.91	1.015
HFD silica/0.5	168.28	0.126	19.99	4.983
HFD silica/0.6	168.89	0.122	13.04	4.840
HFD silica/1	171.12	0.107	9.37	4.314

Table B.5 Adsolubilization of TCE into bonded ODS

System : 15 ml of aqueous solution, 0.7 g of ODS silica (initial concentration of 896.97 ppm, pH 7)

Silica	Equilibrium Concentration (ppm)	Partitioning Coefficient, P_a	Adsolubilization constant, K_S	Adsolubilized TCE (μmoles/g)
ODS silica/0.3	453.56	0.890	200.21	65.818
ODS silica/0.5	396.51	1.162	192.08	75.122
ODS silica/1	287.19	1.985	176.86	92.951
ODS silica/2	243.19	2.524	166.84	100.127
ODS silica/3	226.16	2.790	158.14	102.905
ODS silica/4	221.07	2.877	156.39	103.736

Table B.6 Adsolubilization of TCE into bonded HFD

System : 15 ml of aqueous solution, 0.7 g of HFD silica (initial concentration of 871.73 ppm, pH 7)

Silica	Equilibrium Concentration (ppm)	Partitioning Coefficient, P_a	Adsolubilization constant, K_S	Adsolubilized TCE (μmoles/g)
HFD silica/0.1	738.29	0.181	162.09	21.764
HFD silica/0.5	622.43	0.401	63.58	40.660
HFD silica/0.6	489.48	0.781	83.54	62.342
HFD silica/1.0	465.72	0.872	76.25	66.217

Table B.7 Effect of agitation Speed on stability of the monolayers (pH7, 25°C, 30 min)

Speed no.	Speed (rpm)	C/Co of Bonded ODS	C/Co of Bonded HFD
1	60	1.000	0.985
4	210	0.980	0.978
9	450	0.983	0.978

Table B.8 Effect of agitation time on stability of the monolayers (pH7, 25°C, 210 rpm)

Agitation time (min)	C/Co of Bonded ODS	C/Co of Bonded HFD
30	0.994	0.978
60	0.994	0.972
120	0.993	0.972

Table B.9 Effect of pH on stability of the monolayers (210 rpm, 25°C, 30 min)

pH	C/Co of Bonded ODS	C/Co of Bonded HFD
4	3.15	0.992
7	3.17	0.980
10	3.16	0.984

Table B.10 Effect of temperature on stability of the monolayers (210 rpm, pH7, 30 min)

Temperature (°C)	C/Co of Bonded ODS	C/Co of Bonded HFD
25	0.995	0.978
50	0.994	0.975
70	0.998	0.969

Table B.11 Effect of ozone concentration on stability of bonded ODS (pH7)

Time (min)	C/Co at 150 g O_3/m^3	C/Co at 100 g O_3/m^3	C/Co at 70 g O_3/m^3
20	0.909	0.968	0.983
40	0.823	0.900	0.953
60	0.712	0.828	0.904

Table B.12 Effect of ozone concentration on stability of bonded HFD (pH7)

Time (min)	C/Co at 150 g O_3/m^3	C/Co at 100 g O_3/m^3	C/Co at 70 g O_3/m^3
20	0.988	0.988	0.991
40	0.970	0.973	0.979
60	0.940	0.955	0.970

Table B.13 Effect of pH under ozone condition on stability of bonded ODS (O_3 concentration of 150 g O_3/m^3)

Time (min)	C/Co at pH 4	C/Co at pH 7	C/Co at pH 10
20	0.941	0.909	0.896
40	0.876	0.823	0.792
60	0.762	0.712	0.704

Table B.14 Effect of pH under ozone condition on stability of bonded HFD (O_3 concentration of 150 g O_3/m^3)

Time (min)	C/Co at pH 4	C/Co at pH 7	C/Co at pH 10
20	0.985	0.988	0.985
40	0.955	0.970	0.958
60	0.904	0.940	0.934

B.2 Sample calculations

Referring to the ODS silica/0.3 in Table B.1

B.2.1 Initial concentration of ODS

$$\text{From initial concentration} = \frac{\text{Mole of ODS}}{\text{Volume}}$$

Since density of ODS = 0.984 g/ml

MW of ODS = 387.94 g/mole

So Mole of ODS $= \frac{0.3*0.984}{387.94}$ $\frac{(\text{ml})(\text{g/ml})}{(\text{g/mole})}$

$= 761$ μmole

Volume $= 0.183$ liter

initial concentration $= \frac{761}{0.183}$ $\frac{(\mu\text{mole})}{(\text{liter})}$

$= \mathbf{4220.42}$ **μM**

B.2.2 Adsorbed ODS

From equation 3.1

$$\text{Adsorbed molecules} = \frac{10^6 * P_c}{1200*n_c - P_c*(M-1)}$$

Since $P_c = 2.22$

n_c = C from ODS+C from CH_3 = 18+2 = 20

M = MW of ODS-(3*MW of Cl)+(2*MW of CH_3)

= 387.94-(3*35.5)+(2*15)

= 311.44

$$\text{Adsorbed ODS} = \frac{10^6 * 2.22}{1200*20-2.22*(311.44-1)} \frac{(\mu g \text{ carbon}/100 g \text{ silica})}{(g \text{ carbon}/100 \text{ mole})}$$

$$= \mathbf{95.23\ \mu moles/g\ silica}$$

B.2.3 Bulk phase concentration

$$\text{From Bulk phase concentration} = \frac{\text{Mole}_{\text{intitial}} - \text{Mole}_{\text{adsorbed}}}{\text{Volume}}$$

Since	$\text{Mole}_{\text{initial}}$	= 4200.42*0.183	(μmole/liter)*liter
		= 768.68	μmole
	$\text{Mole}_{\text{adsorbed}}$	= 95.23*6	(μmole/g)*g
		= 571.38	μmole
	Volume	= 0.183	liter

$$\text{Bulk phase concentration} = \frac{(768.68-571.38)}{0.183} \frac{(\mu mole)}{(liter)}$$

$$= \mathbf{1045.93}\ \mu\mathbf{M}$$

Referring to the ODS silica/0.3 in Table B.3

B.2.4 Partition coefficient (P_a) and adsolubilization constant (K_s)

$$\text{From equation 4.1} \quad P_a = [C^*]/[C_{eq}] = \frac{[C_{initial}]-[C_{eq}]}{[C_{eq}]}$$

Since	$[C^*]$	= 183.63	ppm
	$[C_{eq}]$	= 166.95	ppm

So $P_a = \frac{183.68 - 166.95}{166.95} \frac{(ppm)}{(ppm)}$

$= \mathbf{0.10}$

From equation 4.2 $K_S = P_a/[S]$

Since $P_a = 0.10$

$[S] = \frac{Mole}{Volume}$

$= \frac{(95.23*10^{-6}*0.7)}{0.015} \frac{(mole)}{(liter)}$

$= 0.0044$ M

So $K_S = \frac{0.10}{0.0044} \frac{1}{(M)}$

$= \mathbf{22.55}$ $\mathbf{M^{-1}}$

CURRICULUM VITAE

Name: Ms. Siriporn Jongpatiwut

Birth Date: April 4, 1975

Nationality: Thai

University Education:

1992-1996 Bachelor's Degree of Science in Chemical Engineering
Faculty of Science, Chulalongkorn University