Exam in Surface Engineering KPO040

Date: 2018-03-12

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Allowed material: Calculator approved by Chalmers (Chalmersgodkänd räknare). Paper, pen, eraser and ruler. Data sheet and periodic table are included with the questions. Nothing else is allowed, not even formula collections or handbooks etc.

Grading: Maximum 60 points. Guidelines for grades 3, 4 and 5 are 24p, 36p and 48p.

Hints: Motivate all answers carefully but avoid lengthy and irrelevant text. All answers must be in English.

Question 1 (6p)

Describe at least two types of forces/interactions that typically explain why proteins adsorb to solid surfaces (in water). Also explain what often happens when a water-soluble protein encounters a hydrophobic surface.

Most straightforward are electrostatic and hydrophobic interactions. Also, van der Waals are always present although weaker. Hydrogen bonds may contribute a bit. Covalent bonds are possible. On hydrophobic surfaces water soluble proteins often denature when their hydrophobic interior comes in contact with the surface.

Note that hydrophobic interactions and van der Waals forces are two completely different things.

Mean: 3.7

Question 2

A (6p)

The Langmuir model for binding kinetics can be written as:

$$\Gamma(t) = \frac{\Gamma_{\max} k_{\text{on}} C}{k_{\text{on}} C + k_{\text{off}}} \left(1 - \exp(-(k_{\text{on}} C + k_{\text{off}})t)\right)$$

You are forming a self-assembled monolayer on gold at room temperature by a 1 µM solution of thiolated molecules. The Au-S bond can be treated as irreversible and $k_{on} = 3 \times 10^3$ $M^{-1}s^{-1}$. How long time does it take to cover 50% of the surface according to the model?

Irreversible binding means $k_{off} = 0$ and 50% coverage means $\Gamma/\Gamma_{max} = 0.5$. Solving for the time gives $t = \log(2)/[k_{on}C_0] = 231$ s.

Mean: 5.1

B (4p)

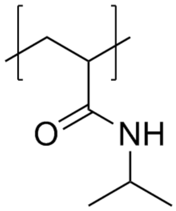
What is the most common explanation why the time you calculated is actually too short (compared to what you would measure in reality)?

The model assumes no influence from mass transport so in reality it might take longer because of the depletion zone (C_0 decreases).

Mean: 2.6

Question 3

You are preparing a polymer brush by end-grafting 60 kg/mol poly(N-isopropylacrylamide):



Afterwards, the film is measured to be 10 nm in the dry state.

A (4p)

Calculate the grafting density. The dry polymer has a density of 1.1 g/cm^3.

The surface coverage is density multiplied by thickness, which gives 1.1×10^{-6} g/cm^2. The mass of one molecule is $60\times10^3/N_A$ g, so there are 1.1×10^{13} molecules on 1 cm^2 (0.11 nm^{-2}).

Mean: 2.5

B (4p)

Determine the height of the brush in water (below the lower critical solution temperature)! You may use the relation:

$$H = \left[\frac{\Gamma abv}{3}\right]^{1/3} N$$

The monomer is 3 Å and the Kuhn length is 5 nm. The excluded volume parameter can be assumed equal to the cube of the monomer size.

Set $v = a^3$. Use Γ from part A. Divide molecular weight with monomer weight (113 g/mol from structure) to get $N = 531$. Inserting all values should give $H = 61$ nm. (Judging from the sidegroup size the assumption $v = a^3$ is maybe not so good if you would do this calculation in reality.)

Mean: 1.8

C (2p)

What is the volume fraction of water inside the brush?

Dry brush is 17% of hydrated thickness so it consists of 83% water (an average value, depends on distance to surface).

Mean 1.0

Question 4 (6p)

In XPS data analysis, so called “sensitivity factors” are used. They are generic, i.e. the same values are used regardless of instrument type etc. What do they represent and what kind of information can be obtained by using them?

The factors represent the probability of different electrons to become emitted due to the x-rays and the tendency of photoelectrons with different energies to give a signal in the detector. With help of those values it is possible to do a RELATIVE quantification of the elements or the COMPOSITION of elements on the surface (no absolute amounts).

Note that XPS bombards the surface with x-rays and that electrons are emitted.

Mean: 1.6

Question 5 (6p)

Describe briefly two ways to measure dynamic contact angle.

Dynamic contact angle can be measured by measuring advancing and/or receding contact angle of a liquid droplet being dispensed by a syringe, tilted base technique where advancing and receding contact angles are determined, by Wilhelmy plate technique using a force tensiometer or sorption technique (Washburn).

Question 6 (4p)

Give four examples of structural factors that affect barrier performance of polymer films?

Crystallinity, polarity, crosslinking, chain stiffness, close packing of molecules, fillers&blends, orientation, liquid crystallinity, external shielding.

Question 7

A (2p)

Draw/explain the cellulose polymer chain structure.

Cellulose is composed of β-D-glucopyranose units linked by 1-4 glycosidic bonds. There is a hydroxyl group in C2, C3 and C6 position. Cellulose polysaccharide consists of glucose repeating units, reducing and non-reducing end group. Alternatively, you can draw the structure.

B (2p)

Describe at least two levels of hierarchical organization of cellulose in plant cell walls.

Levels are cellulose molecule, cellulose chain-chain association, crystalline and disordered regions (amorphous), elemental fibrils, microfibrils, cell wall (and its layers), plant fibers. (add a description to the ones you choose to present).

C (2p)

Explain one way to chemically modify cellulose.

Question 8 (6p)

Plasma treatment can modify surfaces according to three different mechanisms: *Ablation*, *cross-linking* and *activation*. What do they mean? Either describe or provide an example chemical scheme for each.

Ablation means physical etching or milling of molecules from the surface. Cross-linking means introducing covalent bonds between larger molecules in the material, normally polymers, i.e. for plastic materials. Activation means chemical modification of the surface atoms to introduce new groups by reactions with the plasma ions and radicals.

Notes: Ablation is not the same thing as cleaning. It could perhaps be one method for cleaning if you are willing to damage your surface. Cross-linking does not mean that you grow polymers on the surface. You modify the polymers which are already there in the material. Activation does not create radicals on the surface that remain after treatment. The unstable radicals are created in the plasma and cause reactions which generate new groups.

Mean: 2.7

Question 9 (6p)

What is the Vroman effect and why is it important in the context of blood compatibility?

Already adsorbed proteins are replaced by others from solution, usually albumins are replaced by fibrinogen. This is important because covering the surface with fibrinogen is the first step to blood clot formation (followed by cross-linking by thrombin).

Note that the Vroman effect is not the formation of blood clots or implant integration but only related to it.

Mean: 2.4

Helpful constants and data

Boltzmann's constant: 1.381×10^{-23} JK^{-1}

Avogadro's number: 6.022×10^{23} mol^{-1}

Permittivity of free space: 8.854×10^{-12} $m^{-3}kg^{-1}s^4A^2$

Planck's constant: 6.626×10^{-34} m^2kgs^{-1}

Speed of light in vacuum: 2.998×10^8 ms^{-1}

Kelvin temperature scale: 0 °C = 273.15 K

Elementary charge: 1.602×10^{-19} C

Properties of water at room temperature

Density: 1.0×10^3 kgm^{-3}

Dynamic viscosity: 1.0×10^{-3} Pas

Relative permittivity (static field): 80

Refractive index (at 589 nm): 1.333

Surface tension: 7.2×10^{-2} Jm^{-2}

B = Solids Hg = Liquids Kr = Gases Pm = Not found in nature

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	71 Lu 174.967	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	103 Lr (262)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (269)	111 Rg (272)	112 Cn (277)	113 Uut (277)	114 Uuq (277)	115 Uup (277)	116 Uuh (277)		118 Uuo (277)

57 La 138.9055	58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04
89 Ac 232.0381	90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)