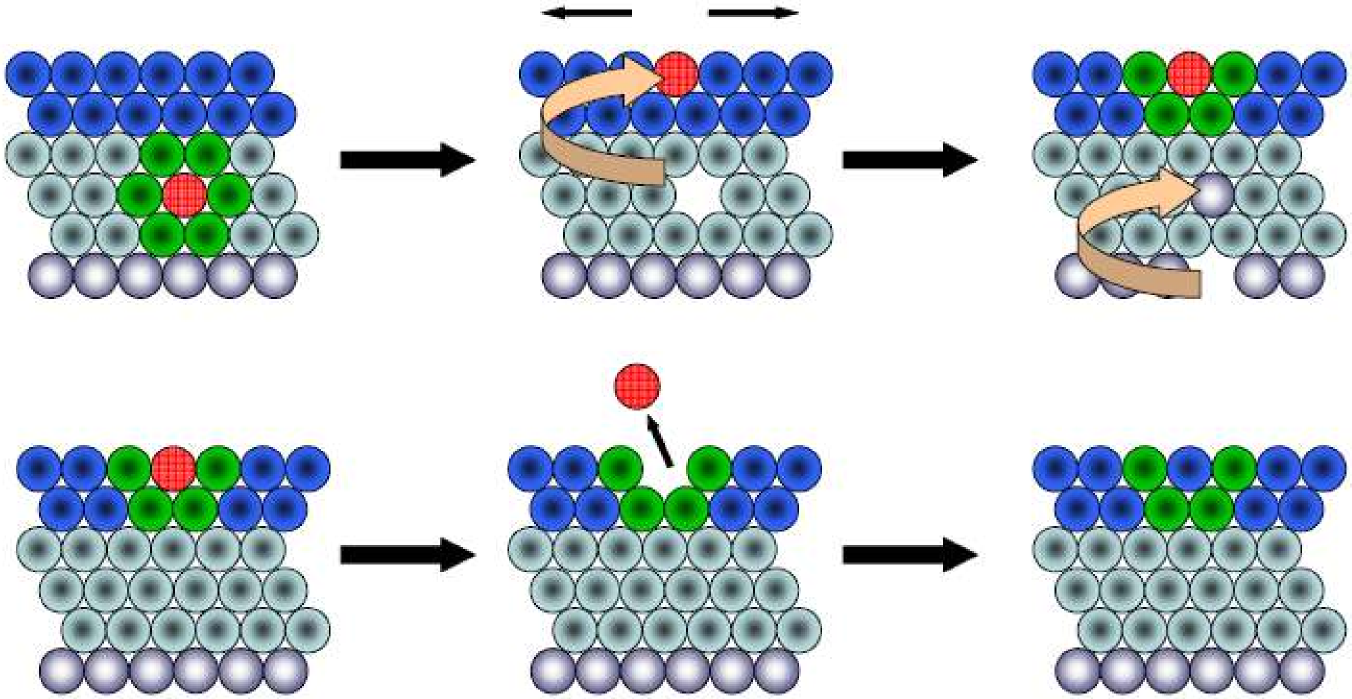
Surface energy

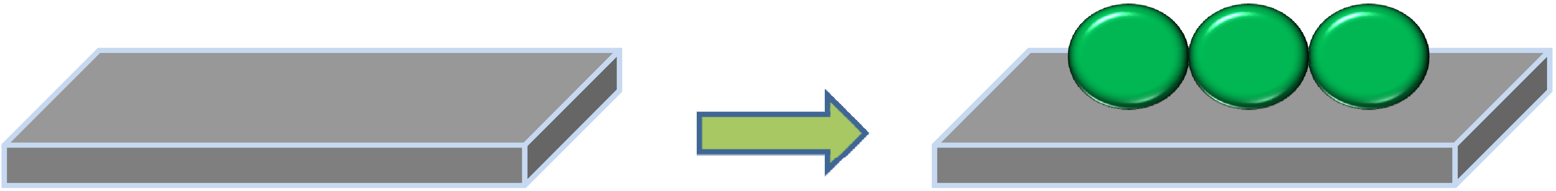
The different energy state between bulk phase and surface phase



The surface is always higher energy than the bulk.
The surface is only a few molecular layer thick (or thin).

So, surface phase is more unstable than bulk phase.

Not only bacterial adhesion but physical adsorption is the spontaneous process in an aspect of energy state.



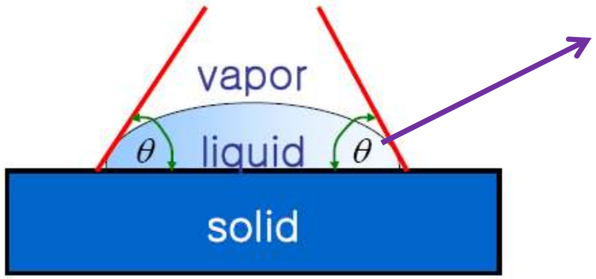
<high energy state>

<low energy state>

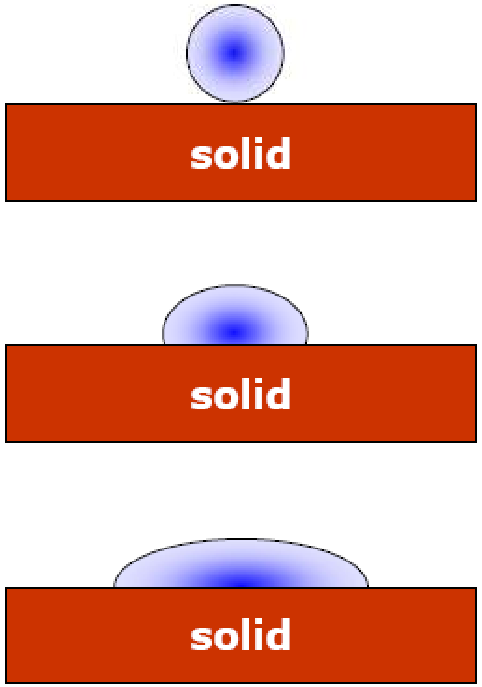
※ Unit of surface energy

mJ/m^2, mN/m, dynes/cm

Contact angle



Contact angle



Non-wetting surface – a sphere has minimum surface to volume

Drop volume is constant

Thus, drop surface area must increase

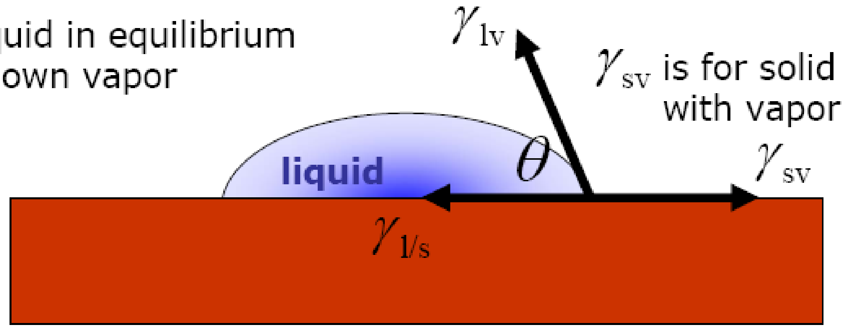
large contact angle
poor wettability

small contact angle
good wettability

Young-Dupre equation

γ_{lv} is for liquid in equilibrium with its own vapor

γ_{sv} is for solid in equilibrium with vapor

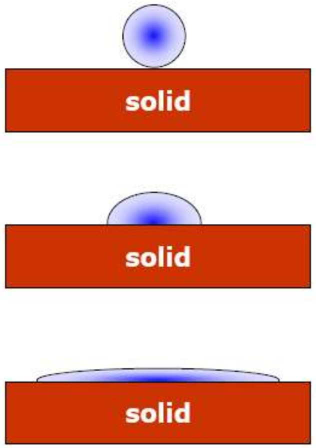


$\gamma_{\mathrm{l/s}}$ is for solid-liquid interface at equilibrium

$$\boxed{\gamma_{\mathrm{sv}} = \gamma_{\mathrm{l/s}} + \gamma_{\mathrm{lv}} \cos\theta}$$

(Young-Dupre Eqn)

Relation between contact angle and wettability



$\theta = 180° \quad \cos\theta = -1$

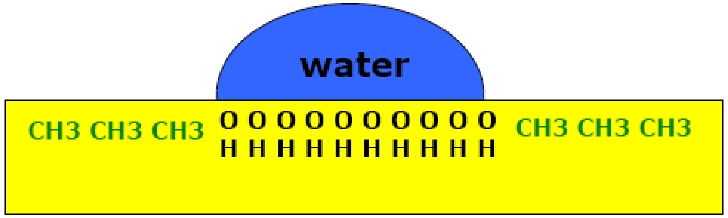
$\theta = 90° \quad \cos\theta = 0$

$\theta = 0° \quad \cos\theta = 1$

- Contact angle
  - Static contact angle
  - Dynamic contact angle
    - Advancing contact angle
    - Receding contact angle

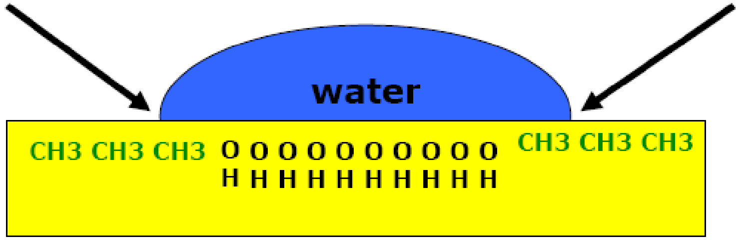
Advancing contact angles (in air) sense the hydrophobic portion of surface properties

Water drop on surface at equilibrium



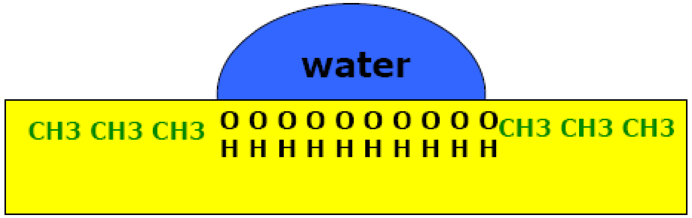
Add water to the drop (advancing)

Drop probes hydrophobic regions and θ_{adv} is high.



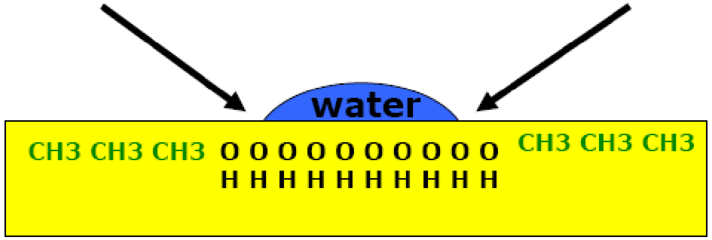
Receding contact angles (in air) sense the hydrophilic portion of surface properties

Water drop on surface at equilibrium



Remove water to the drop (receding)

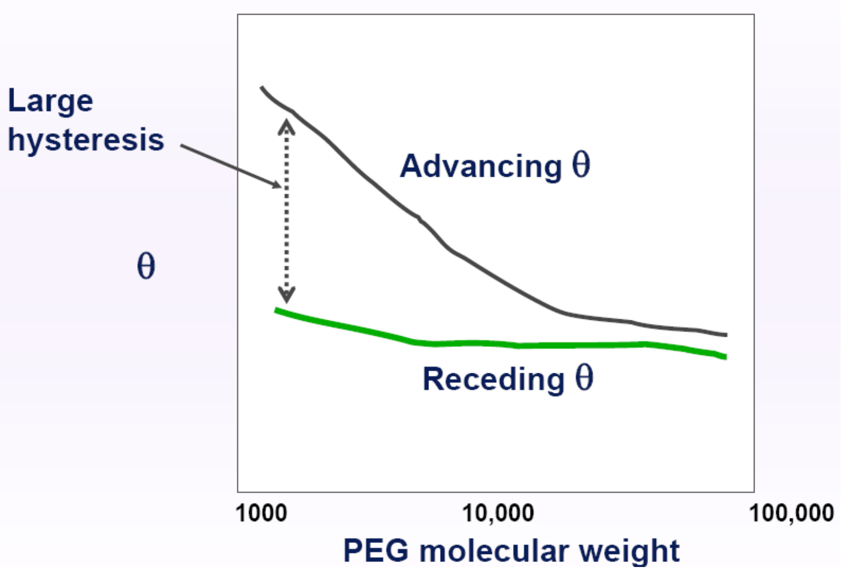
Drop is held back by hydrophilic regions and θ_{adv} is high.



The hydrophobicity of surfaces is reflected in static contact angle, but other properties like surface roughness are contained in the concept of dynamic contact angle.

※ CAH (contact angle hysteresis)

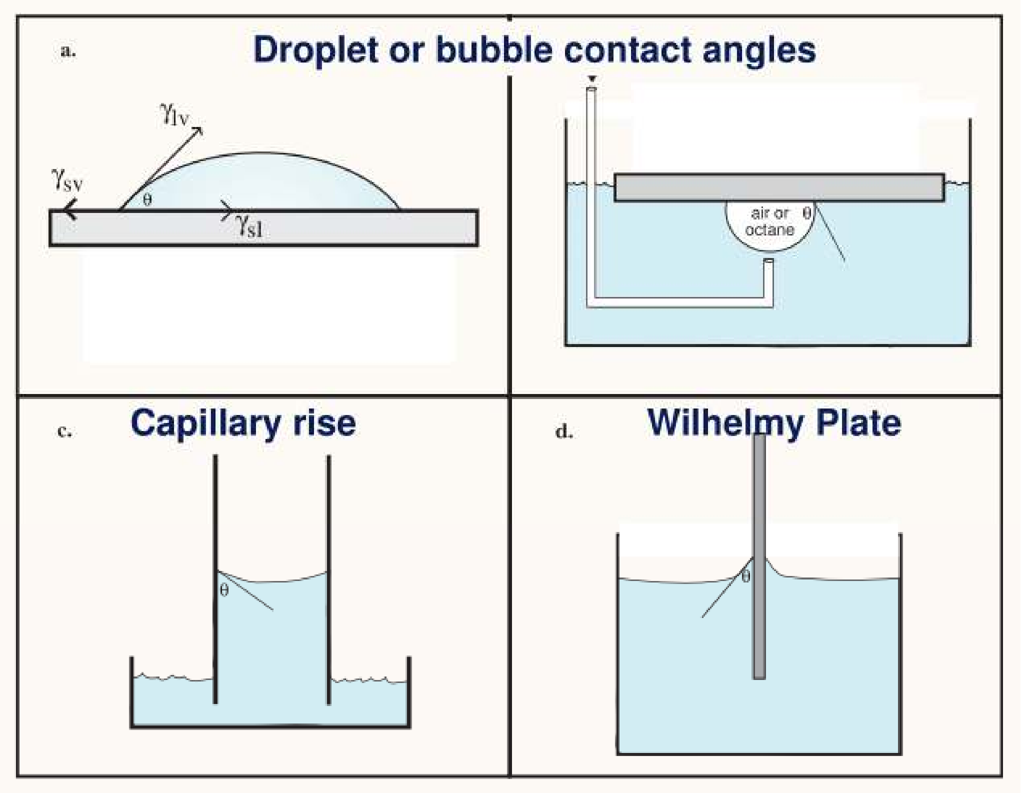
- ~ Difference bewteen advancing contact angel and receding contact angle
- ~ It provide the thermodynamic stability of surfaces.
- ~ CAH is increased with decreasing stability of surfaces.



Contact angle on hydrogels made by crossliking three-arm PEG acrylate of different PEG MWs

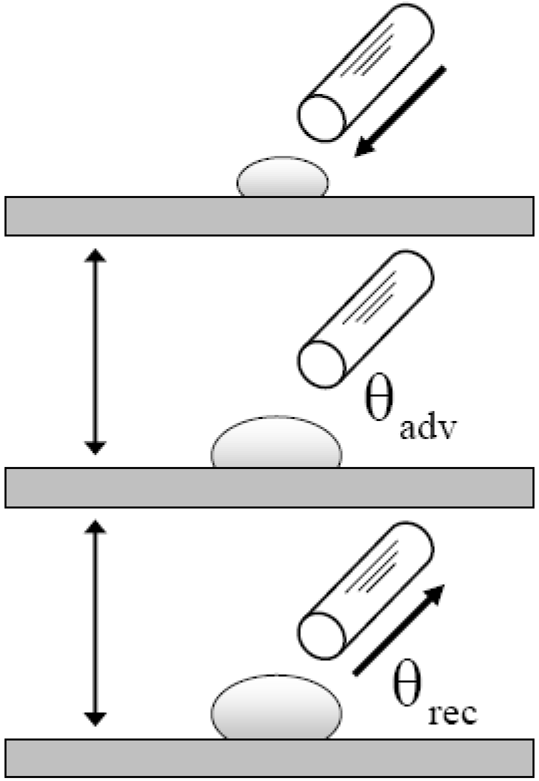
Drumheller and Hubbell, J. Bioed. Mater. Res. 29, 207 (1995)

Measuring contact angle



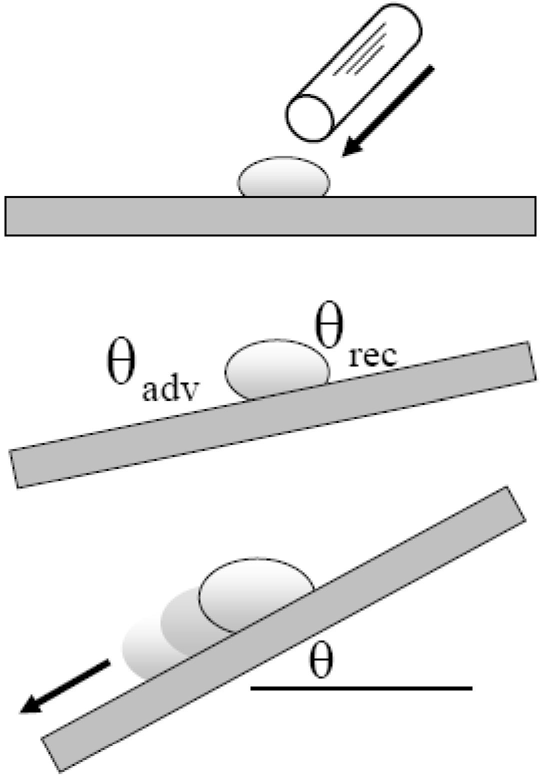
Goniometer for measuring contact angle

Measuring dynamic contact angle



Advancing (θ_{adv}) and receding (θ_{rec}) contact angles

<Captive drop method>



Tilting plane gives both advancing and receding contact angles in same drop.

<Tilting method>

Critical surface tension by Zisman plot

~ A concept developed in the 1960`s by Walter Zisman

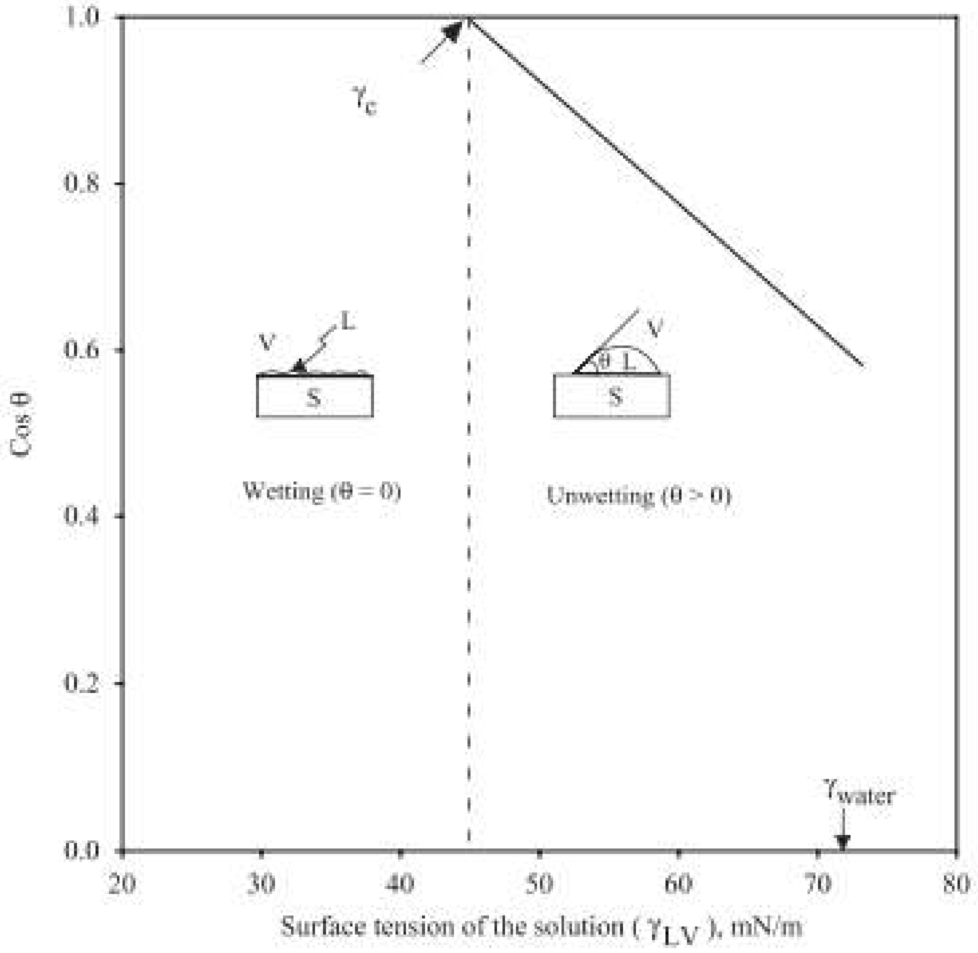
~ The surface tension of a liquid that would completely wet the solid of interest.

~ Surface energy of surface can be expressed by critical surface tension.

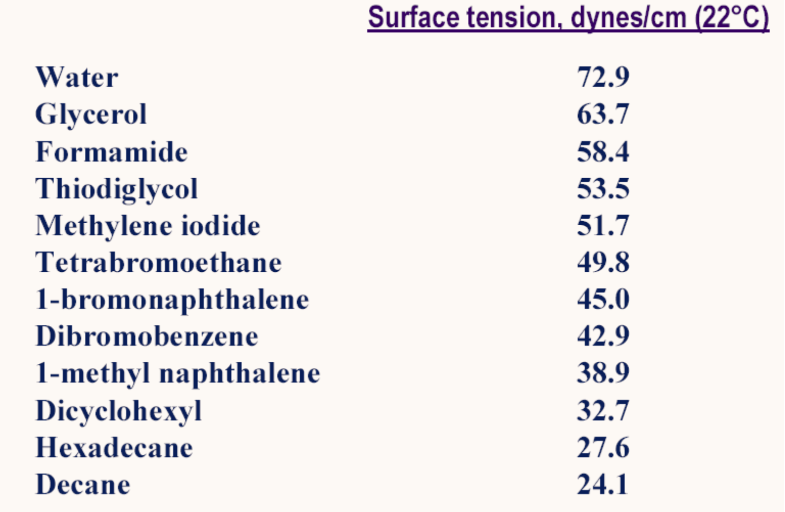
~ Low critical surface tension means that the surface has a low energy.

~ Measure θ_{adv} on one surface for a series of liquids varying in surface tension

Plot cos θ_{adv} vs. γ_{lv}
Extrapolate to cos θ_{adv} = 1.0 (θ_{adv} = 0˚)
Define γ_c = γ_{lv} at cos θ_{adv} = 1.0 (θ_{adv} = 0˚)



The determination of the critical surface tension of a solid by Zisman's contact angle measurement approach (U.Ulusoy, M. Yekeler, 2004)



	Surface tension, dynes/cm (22°C)
Water	**72.9**
Glycerol	**63.7**
Formamide	**58.4**
Thiodiglycol	**53.5**
Methylene iodide	**51.7**
Tetrabromoethane	**49.8**
1-bromonaphthalene	**45.0**
Dibromobenzene	**42.9**
1-methyl naphthalene	**38.9**
Dicyclohexyl	**32.7**
Hexadecane	**27.6**
Decane	**24.1**

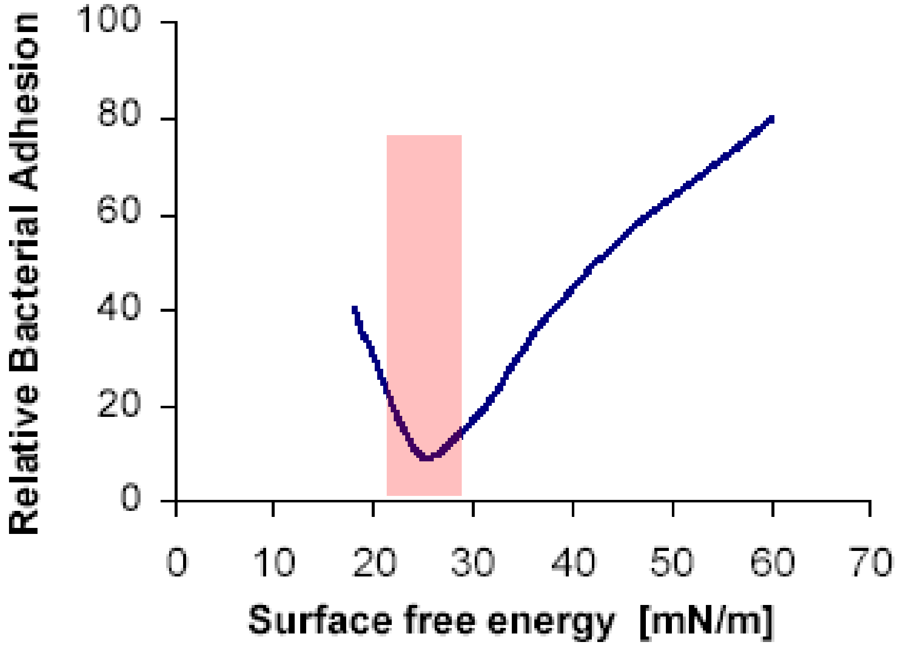
<surface tension of liquids used to determine CSTs>

Bacterial adhesion vs. surface energy

R. E. Baier (1970's)

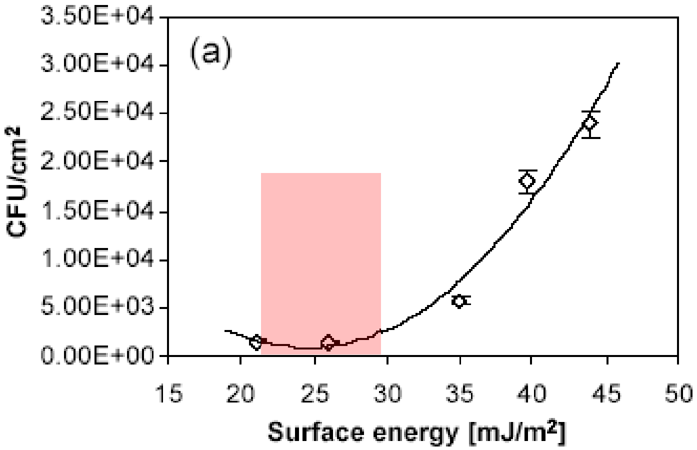
"Bacterial adhesion might be minimum on the surface which has

20-30 mN/m of surface energy." → Theta surface

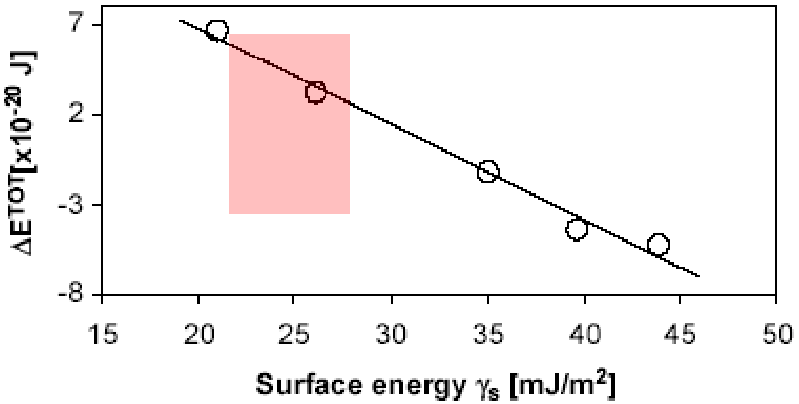


Baier curve (Q.Zhao et al., 2005)

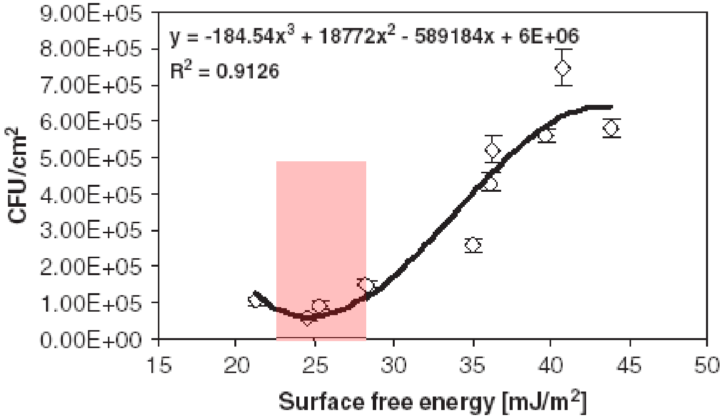
Experimental support of *Baier* curve



Effect of surface energy on E. coli attachment
(Y. Liu et al., 2005)



Total interaction energy vs surface energy
(Y. Liu et al., 2005)



Effect of surface free energy on E. coli adhesion
(Q. Zhao et al., 2007)

※ Limitation of *Baier* curve

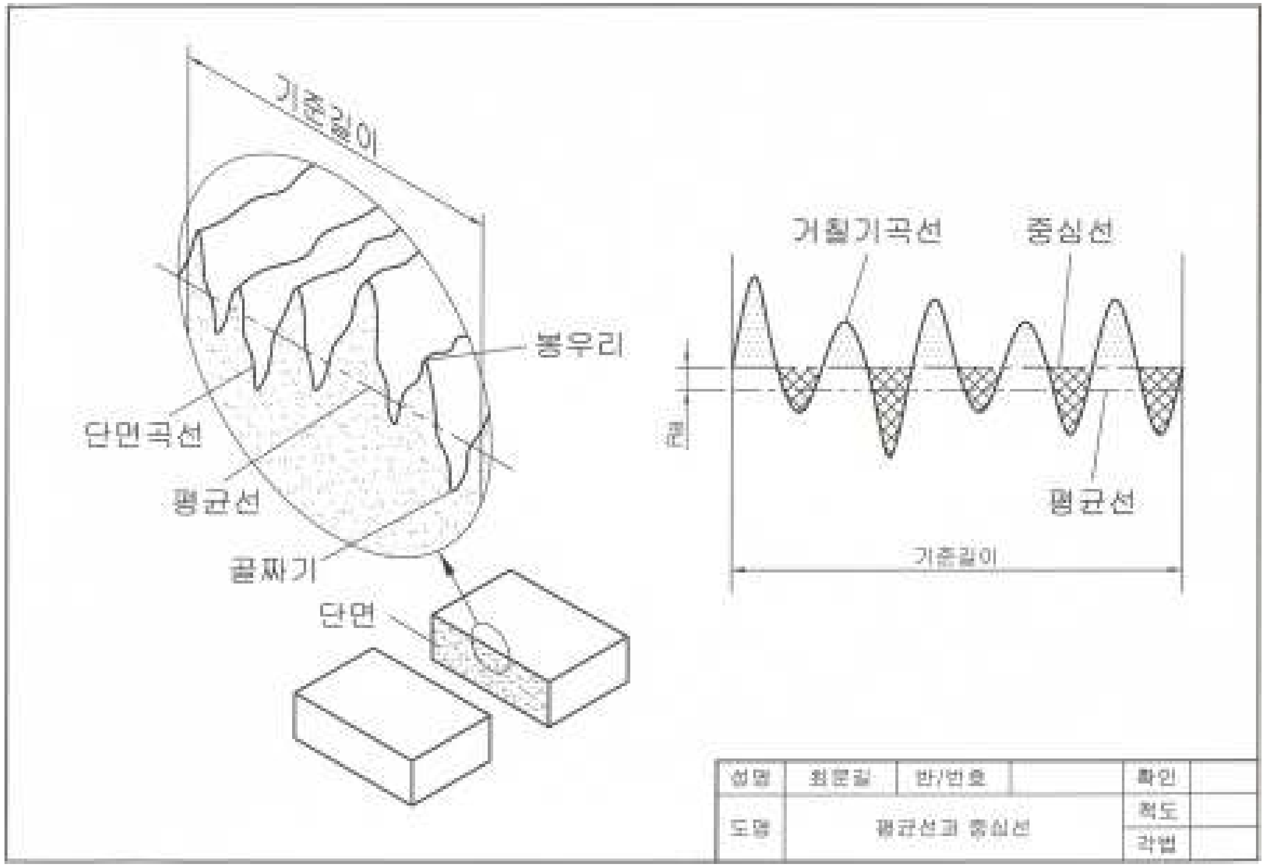
- ~ Experiments of Baier was performed in biological condition like blood vessel, calf serum system where the formation of conditioning film could be occurred.

- ~ Unclear theoritical (physico-chemical) explanation.

- ~ Surface energy of the substratum used in experiment was a range of 20-50 mN/m. Experimental results of substratum which have 0-20 mN/m (superhydrophobic) will be needed.

Surface roughness

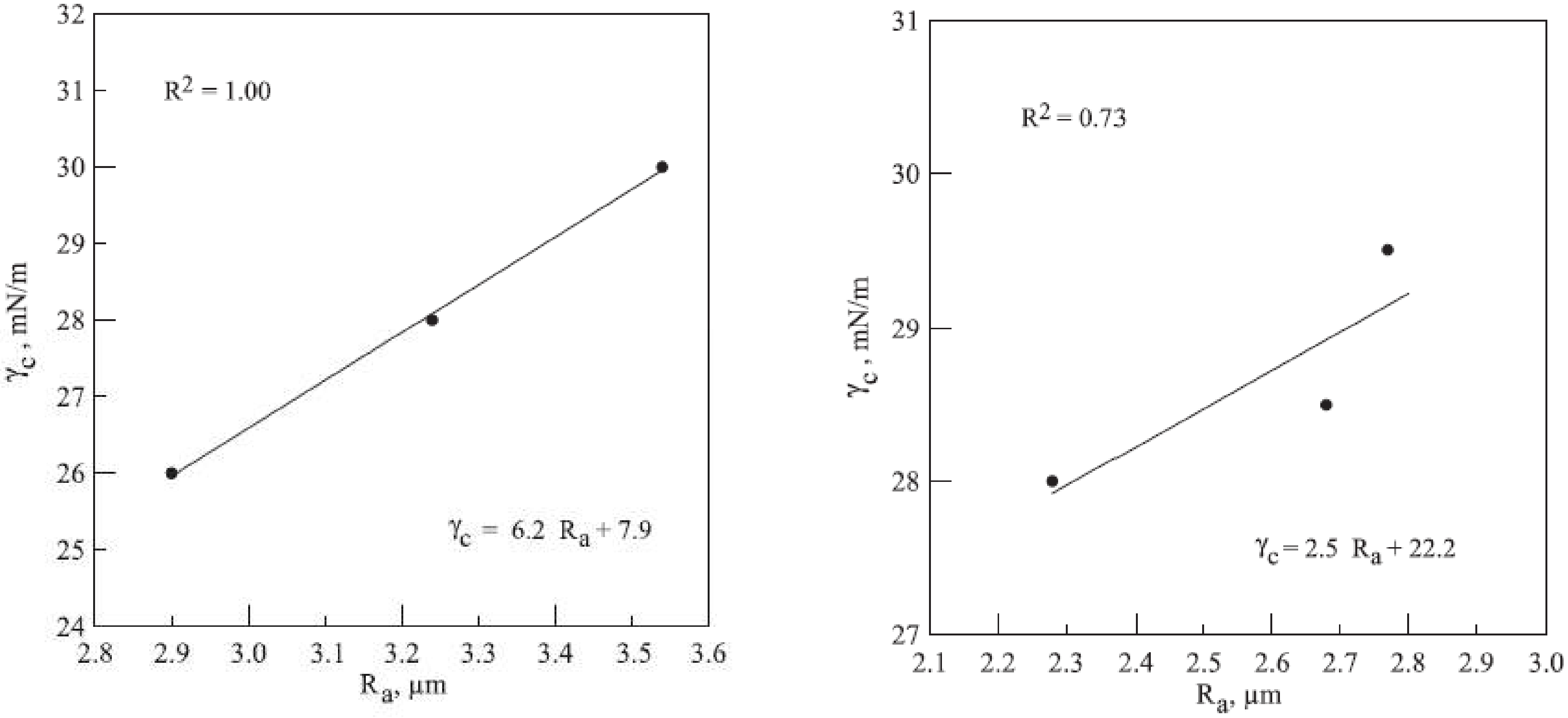
" A measure of the texture of a surface "



Surface roughness curve
http://www.ustech.hs.kr/wbi2/grapic1/UnitK/UnitK1.asp

Surface energy could be influenced by surface roughness

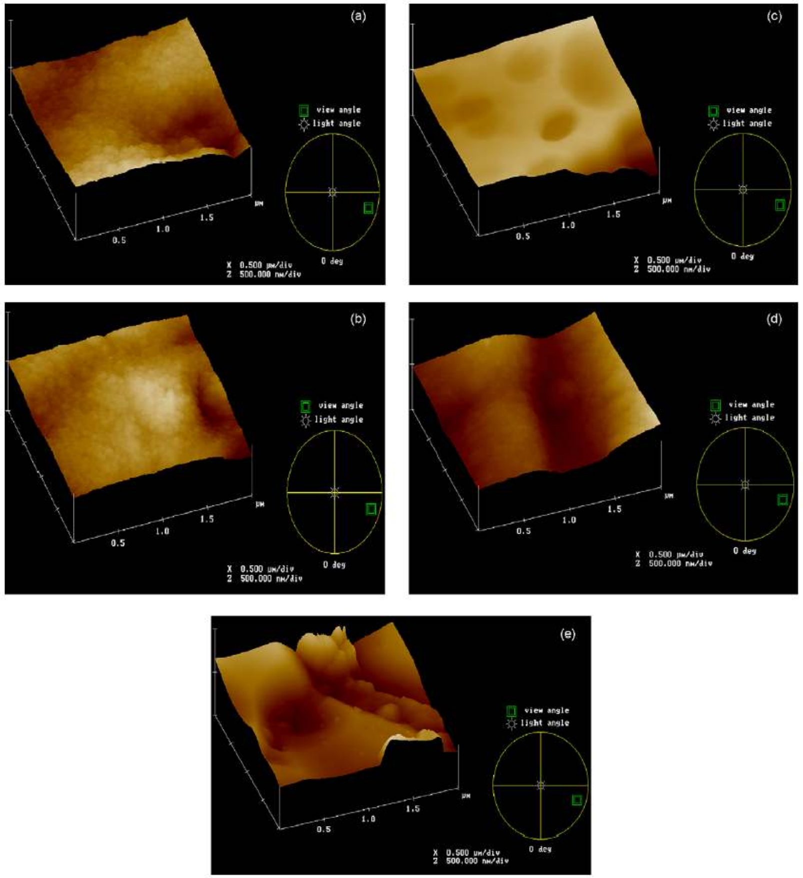
"As the surface roughness increase, the surface energy increase as well"



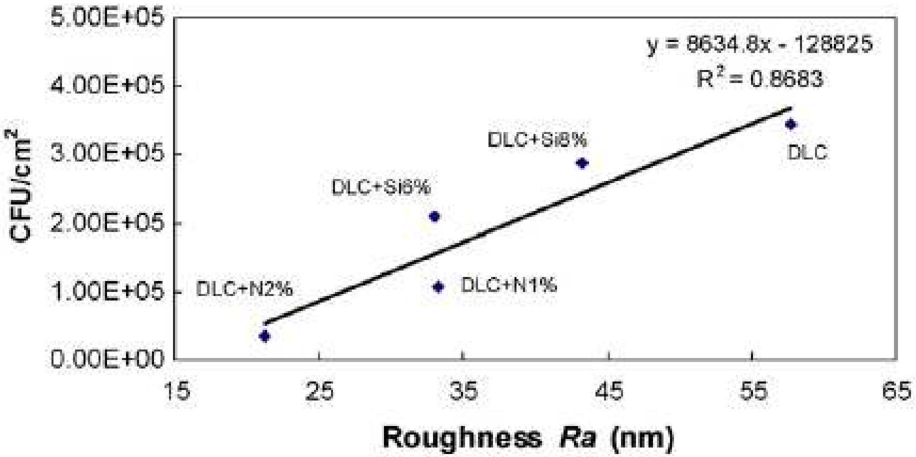
Variation of the critical surface tension with the Ra value for calcite, barite mineral
(U. Ulusoy, M. Yekeler, 2004)

Bacterial adhesion vs. surface roughness

Small surface roughness inhibit the bacterial adhesion.



AFM images of the modified DLC coatings at
(a) 1% N-doped DLC, (b) 2% N-doped DLC, (c) 6% Si-doped DLC, (d) 8% Si-doped DLC and (e) pure DLC. (C. Liu et al., 2008)



Bacterial adhesion vs surface roughness of the DLC coating (C. Liu et al., 2008)

What is the DLVO theory?

DLVO (Deryaguin, Landau, Verwey, and Overbeek) theory: theory of colloid stability
~ Stability of colloidal particle can be explained by balance of attractive force induced by van der Waals and repulsive force induced by electric double layer.
~ the stability of colloid particles is determined by their electrostatic interaction and long-range van der Waals force

Extended DLVO theory: hydrophobic interaction is added!

particle-particle interaction and coagulation, sedimentation and filtration,

being applied to explain the cell adhesion! A cell is treated as a colloid particle!

$$V_{TOT} = V_A + V_R$$

V_{TOT} (net interaction)

V_A (van der Waals interaction)

V_R (electrical double layer interaction)

$$V_A = -\frac{Ar}{6d}$$

A (Hamaker constant)

d (seperation distance between cell & substratum)

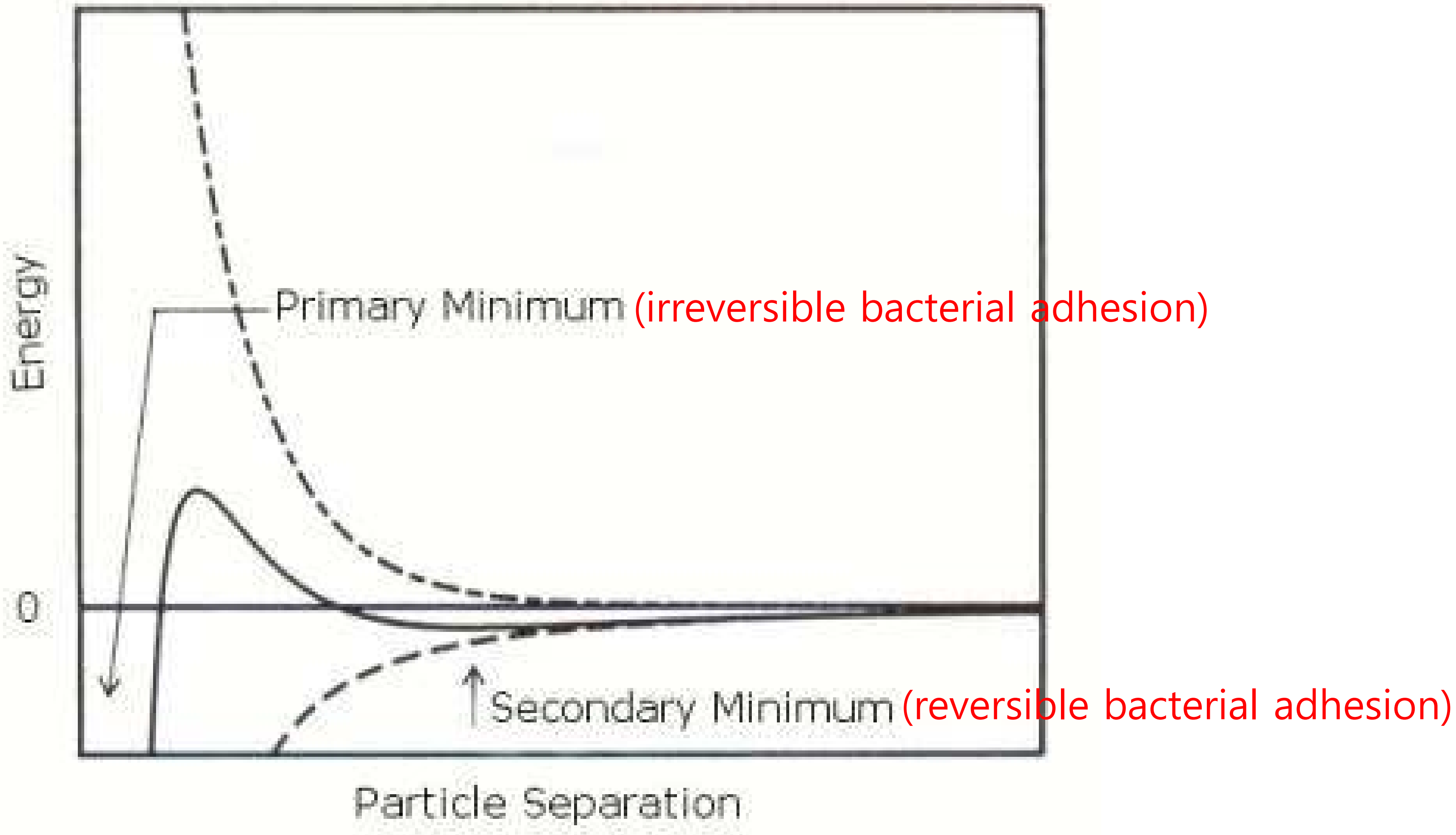
r (radius of the cell)

$$V_R \propto \Psi^2 e^{-\kappa d}$$

Ψ (surface potential)

d (distance between cell & surface)

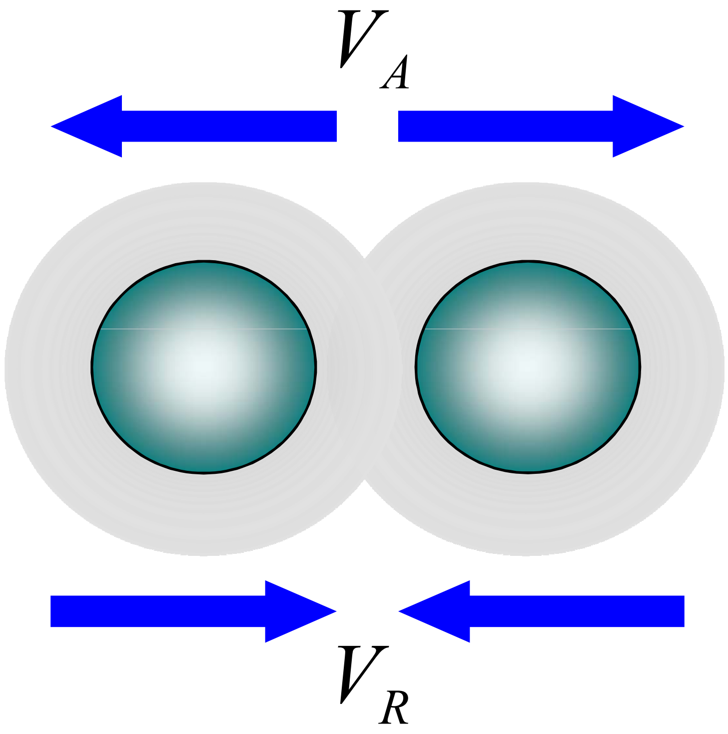
κ (debye length)



Schematic diagram of the variation of free energy with particle separation at higher salt concentrations showing the possibility of a secondary minimum. (www.malven.com)

DLVO Theory

"The harmony between attraction and repulsion results in adsorption."



▨ (Particle)

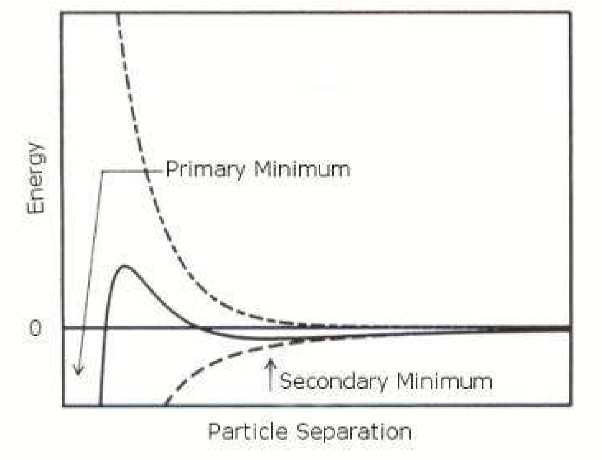
▨ (Electrical double layer)

$$\Delta G^{TOT} = \Delta G^{LW} + \Delta G^{EL}$$

ΔG^{TOT} (Net interaction)

ΔG^{LW} (van der Waals interaction)

ΔG^{EL} (Electrical double layer interaction)



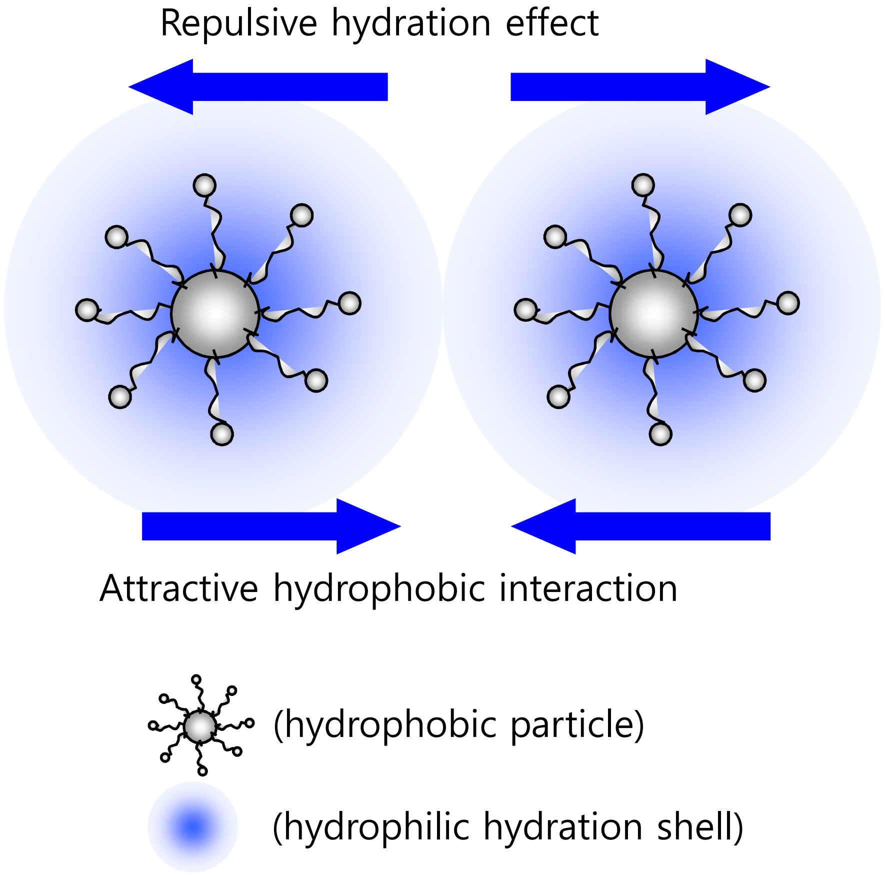
(www.malven.com)

Extended DLVO Theory

"Classical DLVO theory + acid/base interaction = Extended DLVO theory"

$$\Delta G^{TOT} = \Delta G^{LW} + \Delta G^{EL} + \Delta G^{AB}$$

ΔG^{AB} (acid/base interaction; electron donating and electron accepting interaction in aqueous solutions, attractive hydrophobic interaction, repulsive hydration effect)



Repulsive hydration effect

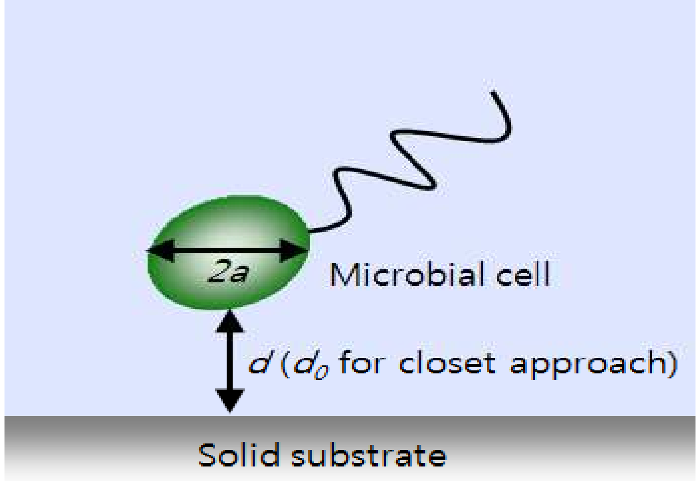
Attractive hydrophobic interaction

(hydrophobic particle)

(hydrophilic hydration shell)

Example: Microbial adhesion to surface

Question: Calculate ΔG_{TOT} of the microbial adhesion to surface A, B, C using extended DLVO theory!



$$\Delta G^{LW}(d) = -\frac{A}{6}\left[\frac{a}{d} + \frac{a}{d+2a} + \ln\left(\frac{d}{d+2a}\right)\right]$$

$$\Delta G^{EL}(d) = \pi\varepsilon a(\zeta_1^2 + \zeta_2^2)\left[\frac{2\zeta_1\zeta_2}{\zeta_1^2 + \zeta_2^2}\ln\frac{1+\exp(-\kappa d)}{1-\exp(-\kappa d)} + \ln\{1-\exp(-2\kappa d)\}\right]$$

$$\Delta G^{AB}(d) = 2\pi a\lambda \Delta G_{mws}^{AB}\exp[(d_0 - d)/\lambda]$$

$$A = -12\pi d_0^2 \Delta G_{mws}^{LW}$$

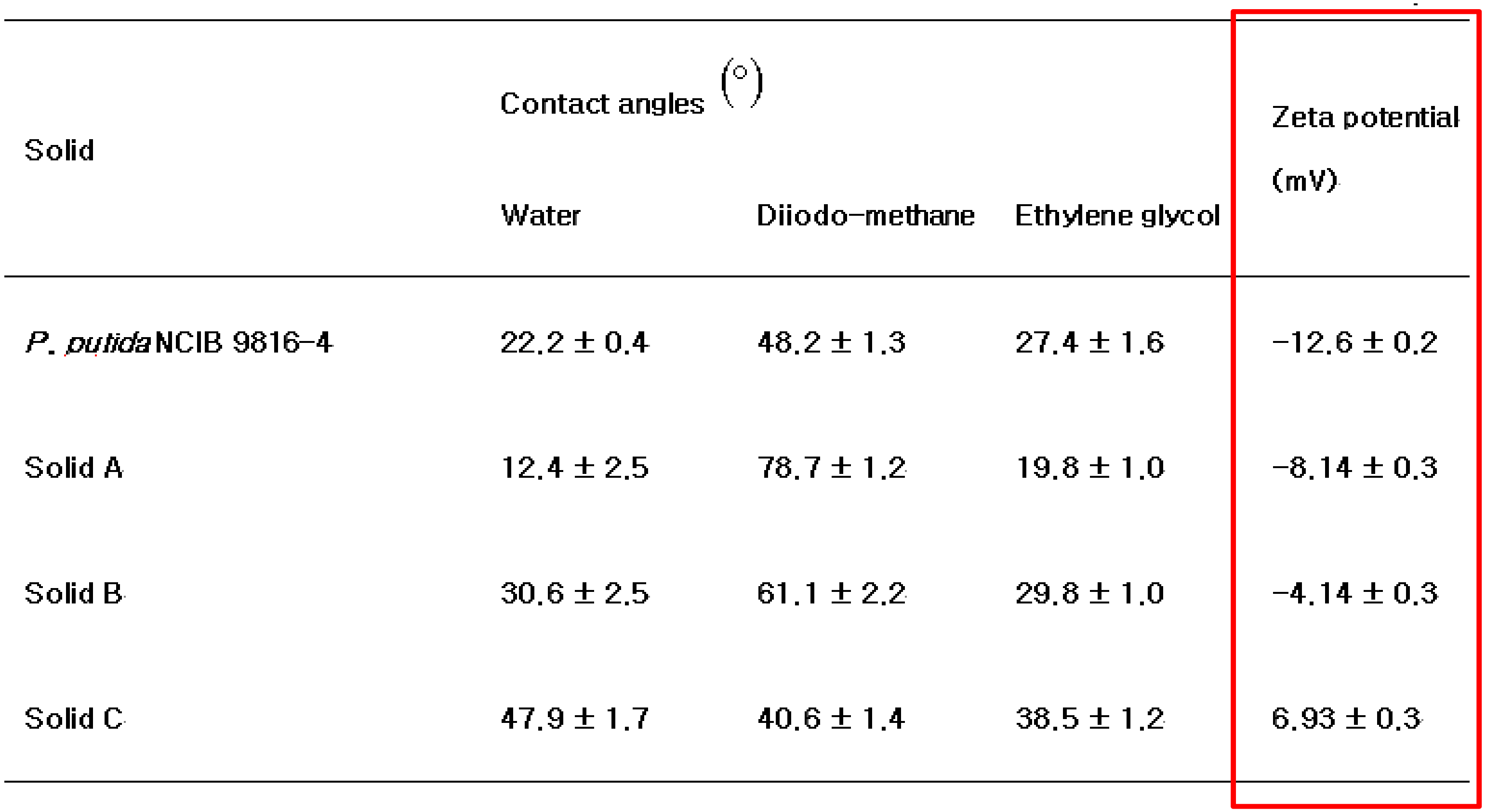
1) $$\Delta G^{EL}(d) = \pi \varepsilon a(\zeta_1^2 + \zeta_2^2)\left[\frac{2\zeta_1\zeta_2}{\zeta_1^2 + \zeta_2^2} \ln \frac{1 + \exp(-\kappa d)}{1 - \exp(-\kappa d)} + \ln\{1 - \exp(-2\kappa d)\} \right]$$

ε Permittivity of medium (water) : 80

κ^{-1} Double-layer thickness : 1000

$\zeta_{1,2}$ Zeta potential (1: bacteria , 2: surface)

Table 1. Contact angles and zeta potentials of microbe and solids



Solid	Contact angles (°)			Zeta potential (mV)
	Water	Diiodo-methane	Ethylene glycol	
P. putida NCIB 9816-4	22.2 ± 0.4	48.2 ± 1.3	27.4 ± 1.6	−12.6 ± 0.2
Solid A	12.4 ± 2.5	78.7 ± 1.2	19.8 ± 1.0	−8.14 ± 0.3
Solid B	30.6 ± 2.5	61.1 ± 2.2	29.8 ± 1.0	−4.14 ± 0.3
Solid C	47.9 ± 1.7	40.6 ± 1.4	38.5 ± 1.2	6.93 ± 0.3

2) $\Delta G^{LW}(d) = -\frac{A}{6}\left[\frac{a}{d} + \frac{a}{d+2a} + \ln\left(\frac{d}{d+2a}\right)\right]$ $\quad A = -12\pi d_0^2 \boxed{\Delta G_{mws}^{LW}}$

A	Hamaker constant related to the properties of the interacting materials
a	Radius of sphere of microbial cell : 8.72*10^{-7} m in this study
d	The distance between the sphere and the plate
d_0	The distance of closest approach between the sphere and the plate : 0.157 nm

$$\Delta G_{mws}^{LW} = -2\left(\sqrt{\gamma_{mv}^{LW}} - \sqrt{\gamma_{lv}^{LW}}\right)\left(\sqrt{\gamma_{sv}^{LW}} - \sqrt{\gamma_{lv}^{LW}}\right)$$

m, w, s, v, l	Subscripts of microbial cell, water, solid substrate, vapor, liquid
ΔG_{mws}^{LW}	Free energy change of apolar or Lifshitz-van der Waals component (mJ/m^2)
γ_{ij}^{LW}	Apolar or Lifshitz-van der Waals component of the surface free energy (mJ/m^2)

3) $\Delta G^{AB}(d) = 2\pi a \lambda \boxed{\Delta G^{AB}_{mws}} \exp\left[(d_0 - d)/\lambda\right]$

λ Correlation length of molecules in medium : 0.6 nm

$$\Delta G^{AB}_{mws} = +2\left(\sqrt{\gamma^{+}_{mv}} - \sqrt{\gamma^{+}_{sv}}\right)\left(\sqrt{\gamma^{-}_{mv}} - \sqrt{\gamma^{-}_{sv}}\right) - 2\left(\sqrt{\gamma^{+}_{mv}} - \sqrt{\gamma^{+}_{lv}}\right)\left(\sqrt{\gamma^{-}_{mv}} - \sqrt{\gamma^{-}_{lv}}\right) - 2\left(\sqrt{\gamma^{+}_{sv}} - \sqrt{\gamma^{+}_{lv}}\right)\left(\sqrt{\gamma^{-}_{sv}} - \sqrt{\gamma^{-}_{lv}}\right)$$

ΔG^{AB}_{mws}	Free energy change of apolar or acid-base component (mJ/m^2)
γ^{+}_{ij}	Electron-accepting parameter of the acid-base component (mJ/m^2)
γ^{-}_{ij}	Electron-donating parameter of the acid-base component (mJ/m^2)

$$\underbrace{\Delta G^{AB}_{mws} \qquad \Delta G^{LW}_{mws}}_{\text{Surface tensions between two phases}}$$

↓

Van Oss`s acid-base approach

Van Oss`s acid-base approach

$$\gamma_i^{TOT} = \gamma_i^{LW} + \gamma_i^{AB}$$

γ^{LW} (Lifshitz-van der Waals apolar component)

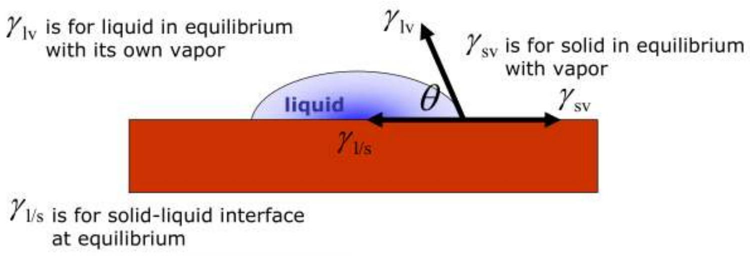
γ^{AB} (Lewis acid-base polar component)

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^{+}\gamma_i^{-}}$$

$\gamma_i^{\pm}$ (Lewis acid-base polar component of I , (+) for e$^-$ acceptor, (-) for e$^-$ donor)

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2(\sqrt{\gamma_{sv}^{LW}\gamma_{lv}^{LW}} + \sqrt{\gamma_{sv}^{+}\gamma_{lv}^{-}} + \sqrt{\gamma_{lv}^{+}\gamma_{sv}^{-}})$$

→ van Oss`s acid-base approach



γ_{lv} is for liquid in equilibrium with its own vapor

γ_{sv} is for solid in equilibrium with vapor

$\gamma_{l/s}$ is for solid-liquid interface at equilibrium

$$\boxed{\gamma_{sv} = \gamma_{l/s} + \gamma_{lv}\cos\theta}$$ **(Young-Dupre Eqn)**

Van Oss`s acid-base approach

$$\gamma_{l/s} = \gamma_{sv} + \gamma_{lv} - 2\left(\sqrt{\gamma_{sv}^{LW}\gamma_{lv}^{LW}} + \sqrt{\gamma_{sv}^{+}\gamma_{lv}^{-}} + \sqrt{\gamma_{sv}^{-}\gamma_{lv}^{+}}\right)$$

Combination of two equations

$$(1+\cos\theta)\gamma_{lv} = 2\left(\sqrt{\gamma_{sv}^{LW}\gamma_{lv}^{LW}} + \sqrt{\gamma_{sv}^{+}\gamma_{lv}^{-}} + \sqrt{\gamma_{sv}^{-}\gamma_{lv}^{+}}\right)$$

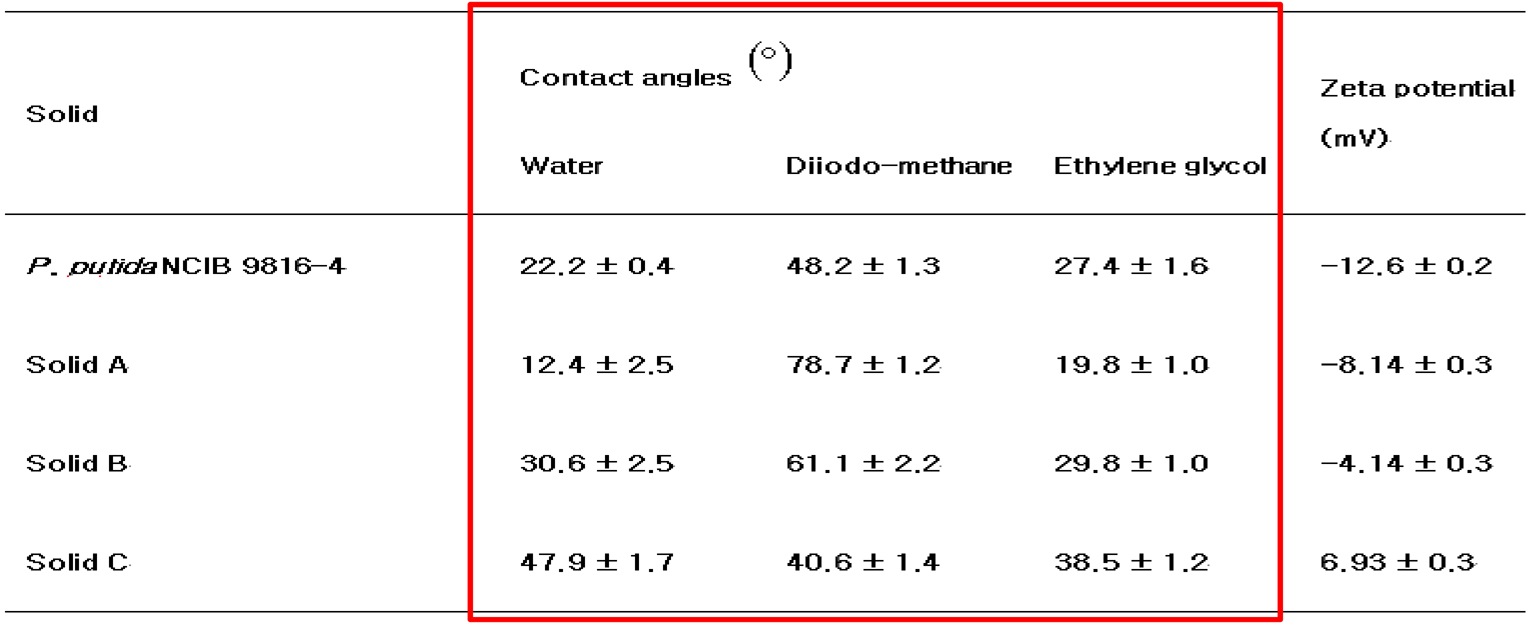
Table 2. Surface energy component of the liquids in the measurement of contact angles

Liquid	γ_{lv}	γ_{lv}^{LW}	γ_{lv}^{AB}	γ_{lv}^{+}	γ_{lv}^{-}
Water	72.8	21.8	51.0	25.5	25.5
Ethylene glycol	48.0	29.0	19.0	1.92	47.0
Diiodomethane	50.8	50.8	0	0	0

[a]: The unit of all the surface energy components is mJ/m^2.

We can obtain parameters of solid substrate; γ_{sv}^{LW}, γ_{sv}^{+}, γ_{sv}^{-} , for three types of liquid.

Table 1. Contact angles and zeta potentials of microbe and solids



Solid	Contact angles (°)			Zeta potential (mV)
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Solid C	47.9 ± 1.7	40.6 ± 1.4	38.5 ± 1.2	6.93 ± 0.3

Case 1. Microbe - Solid A

Solvent 1 : water

$$(1+\cos(radians\,(22.2)))(=2\left(\sqrt{\gamma_{sv}^{LW}\,(21.8)}+\sqrt{\gamma_{sv}^{+}\,(25.5)}+\sqrt{\gamma_{sv}^{-}\,(25.5)}\right)$$

Solvent 2 : diiodomethane

$$(1+\cos(radians\,(48.2)))(=2\left(\sqrt{\gamma_{sv}^{LW}\,(50.8)}+\sqrt{\gamma_{sv}^{+}\,(0)}+\sqrt{\gamma_{sv}^{-}\,(0)}\right)$$

Solvent 3 : ethylene glycol

$$(1+\cos(radians\,(27.4)))(=2\left(\sqrt{\gamma_{sv}^{LW}\,(29)}+\sqrt{\gamma_{sv}^{+}\,(47)}+\sqrt{\gamma_{sv}^{-}\,(1.92)}\right)$$

Three simultaneous equations

↓

$\gamma_{sv}^{LW}, \gamma_{sv}^{+}, \gamma_{sv}^{-}$

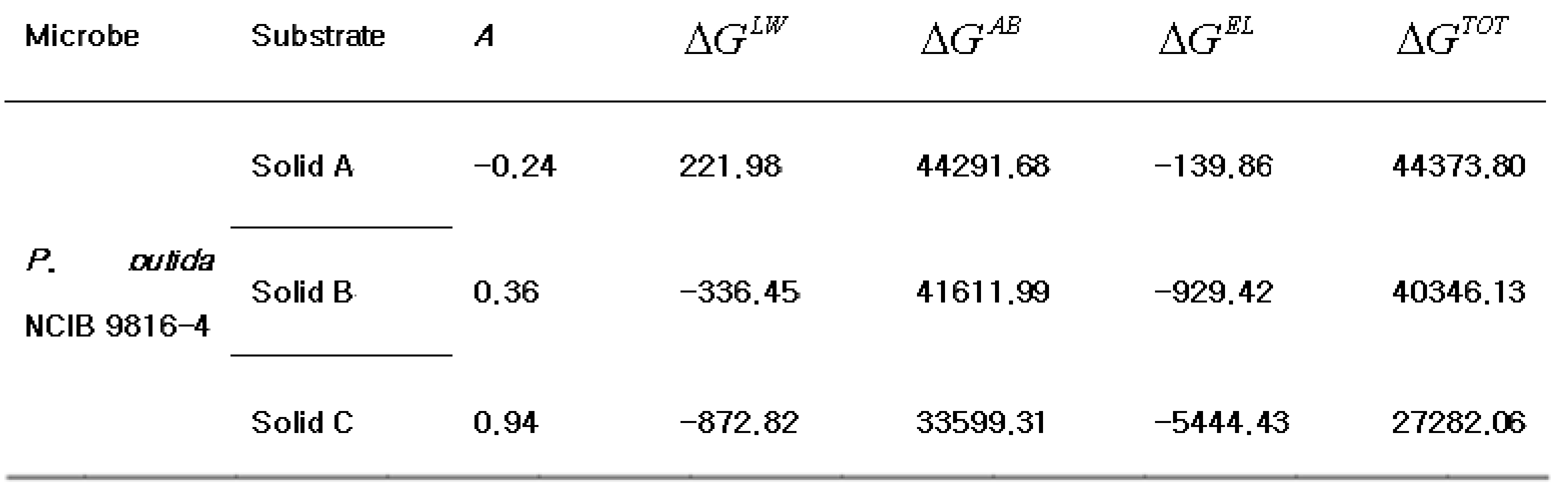
Table 3. Calculation results of solid surface component

Solid	γ_{sv}^{LW}	γ_{sv}^{+}	γ_{sv}^{-}
P. putida NCIB 9816-4	35.27	0.096	65.29
Solid A	18.16	2.92	73.94
Solid B	27.94	0.69	59.20
Solid C	39.31	0.0045	38.15

Table 4. Calculation results of free energy change of adsoption

Microbe	Substrate	ΔG_{mws}^{LW}	ΔG_{mws}^{AB}	ΔG_{mws}^{TOT}
P. putida NCIB 9816-4	Solid A	1.03	53.89	54.92
	Solid B	-1.57	50.63	49.06
	Solid C	-4.07	40.88	36.81

Table 5. Calculation results of free energy change of adsoption by extended DLVO theory



Microbe	Substrate	*A*	ΔG^{LW}	ΔG^{AB}	ΔG^{EL}	ΔG^{TOT}
P. outida NCIB 9816-4	Solid A	-0.24	221.98	44291.68	-139.86	44373.80
	Solid B	0.36	-336.45	41611.99	-929.42	40346.13
	Solid C	0.94	-872.82	33599.31	-5444.43	27282.06

Energy unit : kT (1 kT= 4 * 10^{-21} J)

【 The meaning of these results 】

Calculation of Gibbs free energy change($\Delta G_{TOT,A} > \Delta G_{TOT,B} > \Delta G_{TOT,C}$)

↓

Prediction of microbial adhesion extent (Solid A < Solid B < Solid C)

↓

The most relevant surface

Reference: FEMS Microbiology Reviews 23 (1999) 179-230