Ch. 7 Charged Surface

- Colloid solid dispersion

①분산의 driving force : 입자간 정전기적 반발력(V_R)

②입자의 aggregation force : 입자간 van der waals force(V_A)

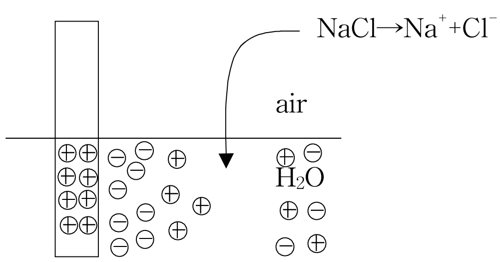
$V_R > V_A \Rightarrow$stabilize　　　　　　$V_R < V_A \Rightarrow$aggregation

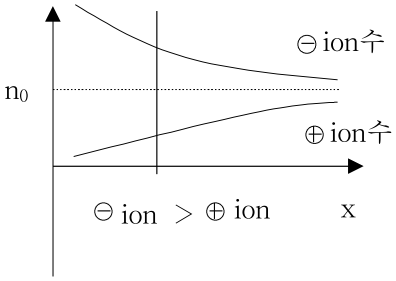
- H_2O내에서 solid particle

1)표면의 ion화

2)Ion의 흡착

3)Ion dissolution





by Boltzman Eq.

$$n_+=n_0\exp(-\frac{ze\psi}{kT})$$

n+:단위 부피당 +ion수　　　　　e: electric charge unit(constant) E/E_0

n0:단위 부피당 NaCl의 분자수　　ψ: electric potential

z: ion의 valency

$$n_-=n_0\exp(+\frac{ze\psi}{kT})$$

net volume charge density

$$\rho=ze(n_+-n_-)=ze\{n_0\exp(-\frac{ze\psi}{kT})-n_0(+\frac{ze\psi}{kT})\}=-2zen_0\sinh(\frac{ze\psi}{kT})$$

by Poisson Eq.

$$\frac{d^2\psi}{dx^2}=-\frac{\rho}{E} \qquad \frac{d^2\psi}{dx^2}=\frac{2zen_0}{E}\sinh\frac{ze\psi}{kT}$$

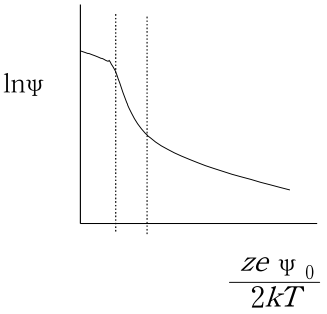
E : permittivity(constant)

boundary condition

$\psi=\psi 0$　　at $x=0$

$\psi=0$　or　$\frac{d\psi}{dx}=0$　　at $x=\infty$

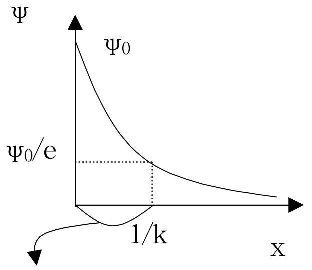
$$\psi=\frac{2kT}{ze}\ln[\frac{1+\gamma\exp(-kT)}{1-\gamma\exp(-kT)}] \qquad \gamma=\frac{\exp(\frac{ze\psi_0}{2kT})-1}{\exp(\frac{ze\psi}{2kT})+1} \qquad k=[\frac{2e^2n_0z^2}{EkT}]^{\frac{1}{2}}$$

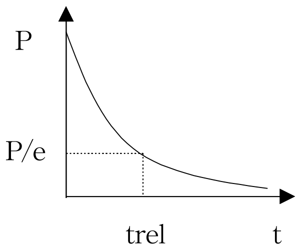


if, $\frac{ze\psi_0}{2kT} \ll 1.0$

$\exp\left(\frac{ze\psi_0}{2kT}\right)=1+\frac{ze\psi_0}{2kT}$

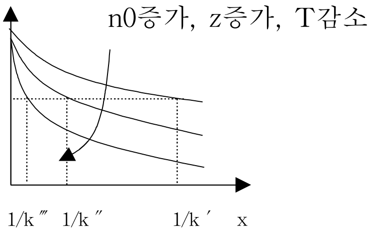
∴ $\psi=\psi_0\exp(-kT)$



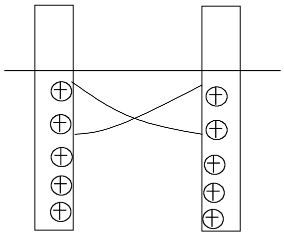


effective double layer thickness (Debye-Hükel length)

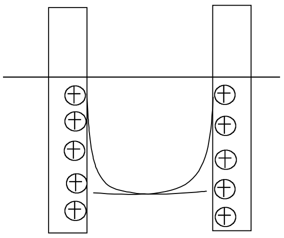
$$k=\left[\frac{2e^2n_0z^2}{EkT}\right]^{1/2}$$



$n_0\uparrow, z\uparrow, T\downarrow \Rightarrow k\uparrow \Rightarrow 1/k\downarrow, \psi/e$



느리게 가라앉음

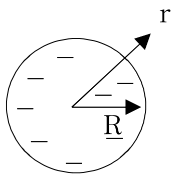


빨리 가라앉음

- Spherical

$$\nabla^2\psi=\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)$$

$$\frac{d^2\psi}{dx^2}=\frac{2zen_0}{E}\sinh\frac{ze\psi}{kT}$$



B.C.1 $\psi=\psi_0$ at $r=R$

$\psi=0$ at $r=\infty$

$\psi=\psi_0\frac{R}{r}\exp(-K(r-R))$

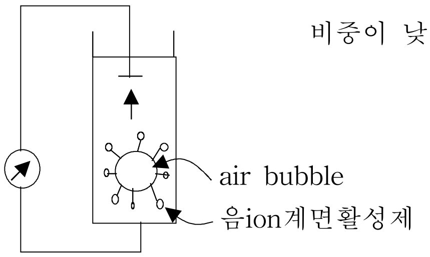
- Electro Kinetic Phenomena

① Electrophoresis(전기영동) : 주어진 외부전압하에서 전하를 띤 콜로이드 입자(무기, 유기, 고분자,단백질)들이 움직이는 현상

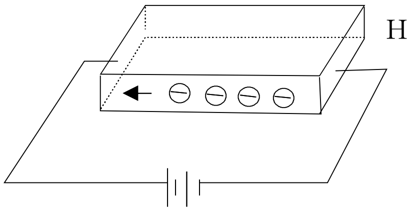
② Electro-osmosis : 외부전압에 의하여 전하를 띤 표면을 따라 ion을 함유한 용액이 흐르는 현상

③ Streaming potential : stationary charged surface를 따라 ion을 함유한 유체를 흐르게 할때 발생되는 전압
⇒강제로 흐르게 하면 potential생김

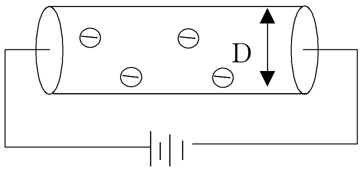
④ Sedimentation potential : charged particle을 액체내부에서 강제로 흐르게 할때 발생되는 전압



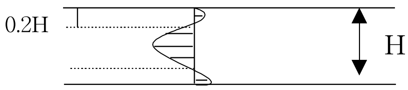
비중이 낮아서 뜨면서 발생

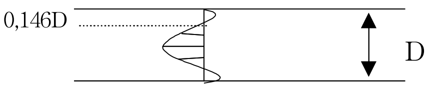


rectangular

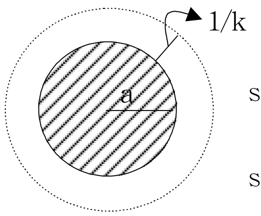


circular





- Zeta-potential (ζ-potential)



shear surface : 입자는 항상 유체층을 갖고 움직인다

shear surface의 potential을 ζ-potential이라 함

① Hukel Eq. (Ka≪1.0, non-conducting particle)

$Ka = \dfrac{a}{\dfrac{1}{k}}$ = ─ 입자의 반경/(effective double layer thickness)

a : 小
1/k : 大 ⇒ 입자size가 작고 천천히 drop

$Q_E \cdot E = 6\pi\eta a V_E = F$(by stoke's law)

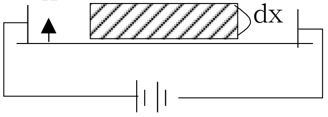
Q_E : net charge of particle surface
E : electric field strength
η : 용액의 점도
V_E : 입자의 이동속도

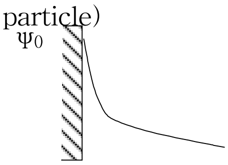
$u_E = \dfrac{V_E}{E} = \dfrac{QE}{6\pi\eta a}$ = electrophoreric mobility

$\zeta = \frac{Q_E}{4\pi E a} - \frac{Q_E}{4\pi E(a+1/k)} = \frac{Q_E}{4\pi E a(1+ka)}$ if Ka≪1.0 (대개 0.1μm이하 입자에겐 적용된다)

$\therefore u_E = \frac{4\pi E a\zeta}{6\pi\eta a} = \frac{\zeta E}{1.5\eta}$ 입자 surface potential ↑, 입자간 반발력도 ↓

② Smoluchowski (Ka≫1.0, non-conducting particle)





plate로 가정

differential segment의 unitwidth에서 force balance

$E\rho dx \cdot 1 = [\eta \frac{dV}{dx}]_{x+dx} - [\eta \frac{dV}{dx}]_x dx$

since $\rho = -\frac{d}{dx}[E\frac{d\psi}{dx}]$ $-E\frac{d}{dx}[E\frac{d\psi}{dx}] = \frac{d}{dx}[\eta\frac{dV}{dx}]$

적분 $-EE\frac{d\psi}{dx} = \eta\frac{dV}{dx} + C_1$ ($\because$ at $x=\infty$, $\frac{d\psi}{dx} = \frac{dV}{dx} = 0$)

적분 $-EE\psi = \eta V + C_2$ B.C. $\psi=0$, $V=0$ at $x=\infty$

$\psi=\zeta, V=-V_E$ at shear surface

$-EE\psi = \eta V$ $\therefore u_E = \frac{V_E}{E} = \frac{\zeta E}{\eta}$

③ Hery Eq. (for conducting as well as non-conducting particle)

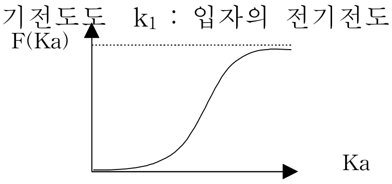
$u_E = \frac{\zeta E}{1.5\eta}[1+\lambda F(Ka)]$

: 전도성이 아주 좋은 용액의 입자는 전기를 통해도 입자 움직이지 않는다

$\lambda = \frac{k_0 - k_1}{2k_0 + k_1}$ k_0 : 용액의 전기전도도 k_1 : 입자의 전기전도도

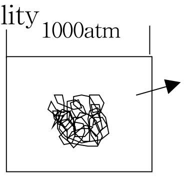
for non-conducting particle $\lambda=1/2$

if $k_1=\infty$ (전기전도도 high) $\lambda=-1$



Chap. 8. Colloidal Stability

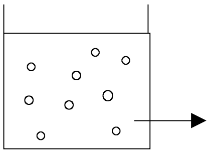
① Sludge 처리



입자사이에 H_2O : 80%

Clay, 미생물 : 20%

② Polyester



homogeneous

250℃ melt

실뽑아냄

- Aggregate 형성

Driving force : vander waals′ attractive force (V_A)

Against force electrostatic repulsive force (V_R)
steric hindrance by polymer
solvation force

- Critical coagulation concentration (CCC)

①salt : particle surface의 electrical property변화 ⇒ 입자간 V_R이 변화

②CCC: colloid분산계에서 colloid입자들을 aggregation시키는데 필요한 salt의 농도

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

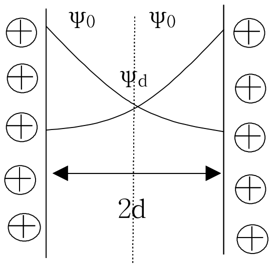
- Interaction Energy=van der waals′ attractive interaction energy
  - electrostatic repulsive energy

cf) $\frac{dE}{dx}=F$ $\quad w=Fdx=dE$

※ for flat plate

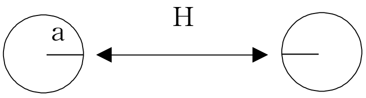
오른쪽 fixed, 왼쪽← : 무한대거리로부터 2d거리까지 가져오는데 하는 일

왼쪽 〃 , 오른쪽꺼 → : 〃 〃



$$Gd=w=-\int_{\psi_d}^{\psi_\infty}\rho d\psi \qquad \rho=ze(n^+-n^-) \qquad V_R=2G_d$$

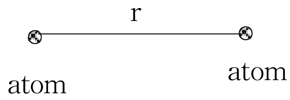
for spherical particle



$$V_R=2\pi E\psi_d^2\exp(-\kappa H)$$

van der waals attractive energy

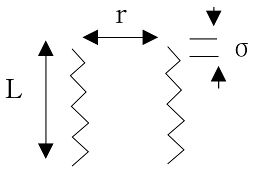
$$w=-\frac{c}{r^6}$$



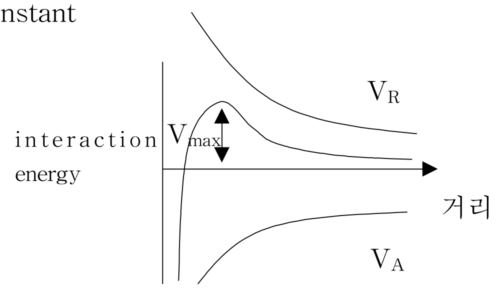
$$V_A=-\frac{Aa}{12H}$$

A : Hamaker constant

polymer chain



$$V_A=-\frac{3\pi AL}{8\sigma^2 r^5}$$



$V_{max}>kT$ ⇒ stable dispersion

$V_{max}<kT$⇒ aggregation

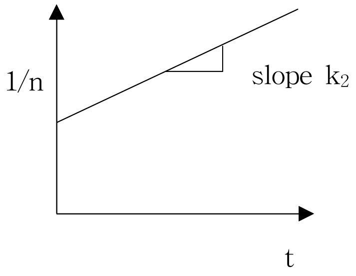
- Kinetics of coagulation

n : 단위부피당 입자수

$$-\frac{dn}{dt} = k_2 n \cdot n = k_2 n^2 \qquad n = n_0 \quad \text{at} \quad t = 0$$

$$-\int_{n_0}^{n} \frac{dn}{n^2} = \int_0^t k_2 dt$$

$1/n - 1/n_0 = k_2 t$



※ Coalter counter

: 입자가 흐르면서 두 전극사이의 전류변화가 생김
  거기서 입자수 측정

- Systems containg lyophilic material

Solvation : solvent분자들이 입자표면에 흡착되어 한입자로 간주되는 현상

Hydration : solvent가 H_2O인 경우

- Ion의 hydration ⇒ surface charge density에 비례
  Bare ionic size : $Li^+ < Na^+ < K^+ < Cs^+$
  Surface charge density : $Li^+ > Na^+ > K^+ > Cs^+$
  Hydrated ionic size : $Li^+ > Na^+ > K^+ > Cs^+$

※입자의 potential E↓⇒쉽게 aggregate가 일어난다

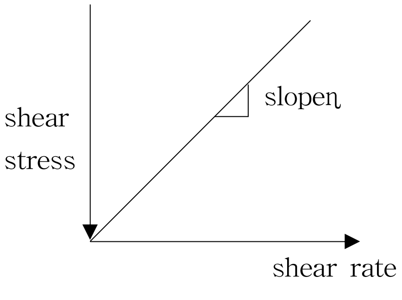
- Salting-out : 용해된 물질이 salt의 첨가에 의하여 석출되는 현상
  Salting-in : 석출된 물질이 salt의 첨가에 의하여 투명한 용액으로 다시 용해되는 현상
  Salting-out power ⇒ $Mg^+ > Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^+ > Na^+ > K^+$
  Salting-in ⇒ NH_4NO_3

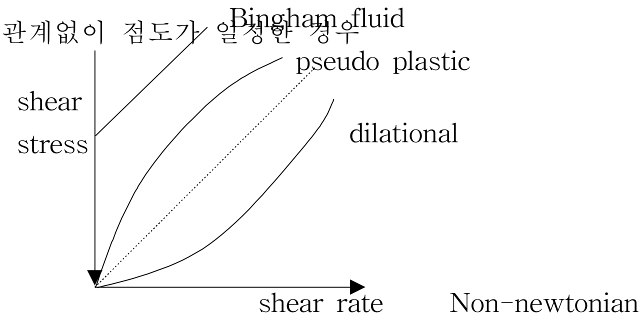
Chap.9 Rheology

물질의 흐름과 변형을 다루는 학문

⇒ rubber, plastic, food, colloid용액

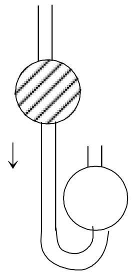
- Colloid system의 Rheology에 영향을 미치는 factor
  ① dispersion medium의 점도
  ② particle의 수
  ③ particle size, 모양
  ④ particle-particle 사이의 영향
- Viscosity : 흐름에 저항하는 정도
  for Newtanian fluid : shear rate에 관계없이 점도가 일정한 경우





- Viscosity측정

① Capillary flow method



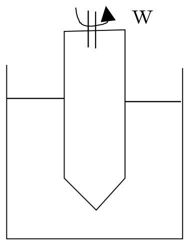
$\eta=\rho kt$

$\eta_1=\rho_1 kt_1$

$\eta_2=\rho_2 kt_2$

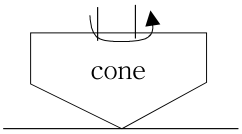
$$\therefore \frac{\eta_1}{\eta_2}=\frac{\rho_1 t_1}{\rho_2 t_2}$$

② Rotational method



$$\eta=\frac{k\Theta}{w}$$

③ Cone-plate viscometer

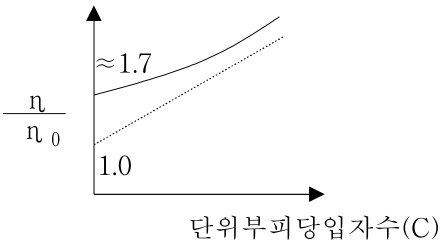


η_0 : viscosity of dispersion medium

η : colloid 용액의 점도

$\frac{\eta}{\eta_0}$=relative viscosity

$\lim_{c\to 0}\frac{\eta}{\eta_0}$=intrinsic viscosity

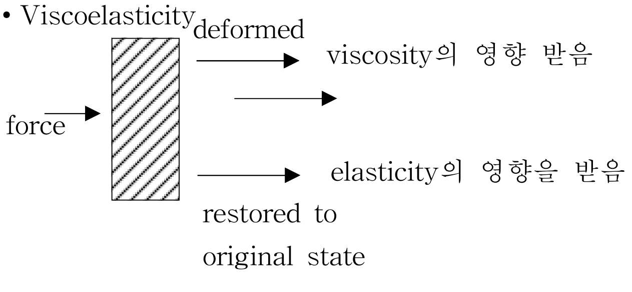


for spherical dilute colloidal system

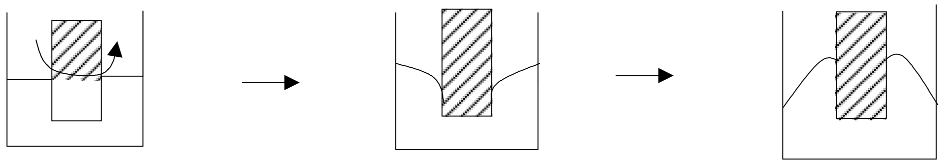
$\eta=\eta_0(1+2.5\Phi)$ $\Phi<0.02$인 경우

$$\Phi=\frac{particle의부피}{medium의부피}$$

- Viscoelasticity



- Weissenburg Effect(polymer)

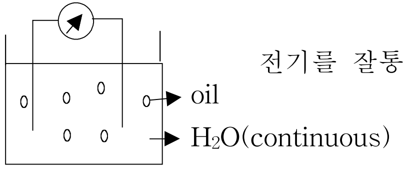


Chap 10. Emulsion & Foam

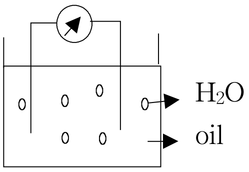
서로 섞이지 않는 유체들에서 하나의 유체가 다른 유체에 drop형태로 dispersion

- Methods to determine the structure of emulsion

1)

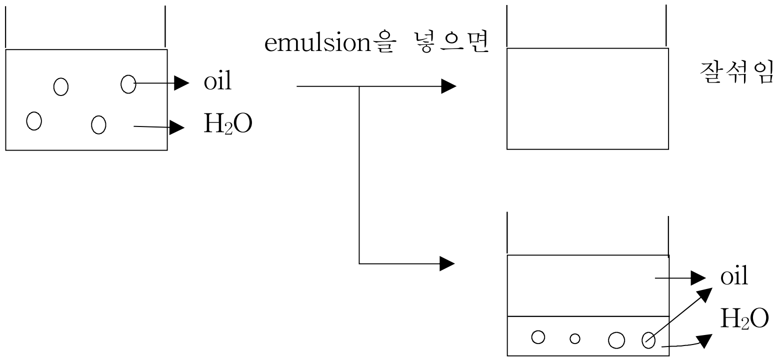


전기를 잘통함



전기를 잘안통함

2)



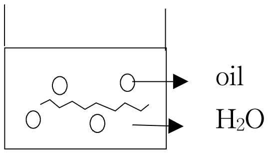
3) $\eta=\eta0(1+2.5\Phi)$

o/w ; oil첨가 점도↑, H_2O첨가 점도↓

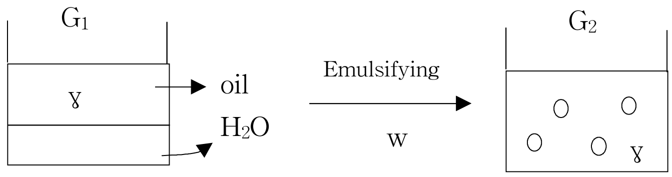
4) 수용성 dye하면 염색 good

ion성 〃 〃 bad

5)



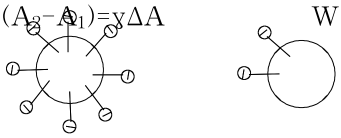
- Emulsifying Agents : variable, 섞어서 쓰기도 함



γA_1 interfacial area↑ γA_2

1)$W=\gamma(A_2-A_1)=\gamma\Delta A$ W=const.

2)



aggregation막아줌

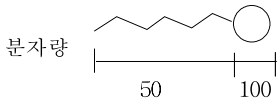
$G_1<G_2$이므로 방향이 반대 방향으로 진행

ordinary solution polymeric solution

flocculation : 각각의 성질을 가지고 있다. low energy로도 분산가능
coagulation : 완전히 하나로 합쳐진 것. high energy가 필요

- HLB Number = $\frac{\text{weight\% of 친수성 group}}{5}$

  : 한분자내의 친유성과 친수성의 balance의 상대적 차이를 지수화



$$HLB=\frac{\frac{100}{150}\times 100}{5}$$

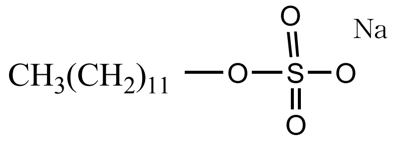
only 친수성 ; HLB=20
only 친유성 ; HLB=0

for nonionic HLB 0 ↕ 친유성, oil-soluble

20 친수성, water-soluble

for ionic
$HLB=\Sigma(\text{hydrophilic number})-\Sigma(\text{hydrophobic number})+7$ (0~40)

ex)


$CH_3(CH_2)_{11}-O-S(=O)_2-O\ Na$

$HLB=(-0.475)+(-0.475)\times 11+38.7+7$

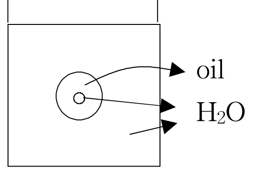
$HLB_{mixture}=fHLB_A+(1-f)HLB_B$ (f : A의 mole fraction)
; 계면활성제는 보통 여러종류 섞어서 많이 사용

HLB values(Bancroft rule)
oil-soluble ⇒ w/o emulsion
water-soluble ⇒ o/w emulsion (oil in water)

- Emulsification Methods : w 가해주는 방법

1)Homogenizer : high-speed mixer
2)Colloid mill
3)High pressure homogenizer
식품원료(물,기름×)

- Multiple Emulsion



w/o/w

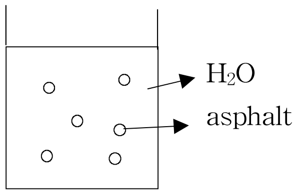
- Rheology of Emulsion

microstructure가 network형성 : 점도↑ for 생산성 cost control

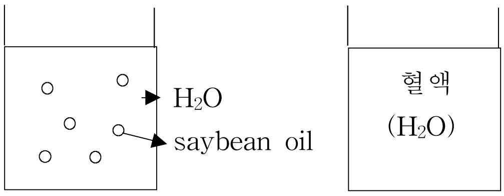
- Application of Emulsion
  - cola
  - paper wax coating

    : candle 수용액내에 60℃에서 melting size 1㎛로 분산

    ⇒ 이 emulsion을 종이에 발라서 물증발 시킴
  - 아스팔트 : 점도↑



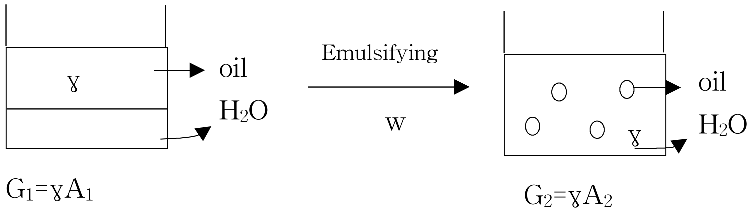
  - medical and pharmaceutical



  - Explosion : 단시간내에 다량의 gas생산 (압력↑)

- Microemulsion

Emulsion ┬ microemulsion : drop size 0.1㎛이하, 투명, 열역학적으로 stable
└ minienulsion
(macro)emulsion : 0.5㎛이상, milky, 열역학적으로 unstable



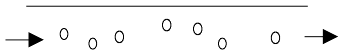
$\Delta G=\gamma(A_2-A_1)$ $\gamma\approx 0$ (or negative)여야 0.1㎛이하로 쪼개짐

∴열역학적으로 stable

emulsion인 경우 $\Delta G>0$이므로 unstable

- Potential application of microemulsion

Soil



oil이 퍼져있는걸 모아주는 거

organic reaction

A와B가 서로 성질이 다를 때