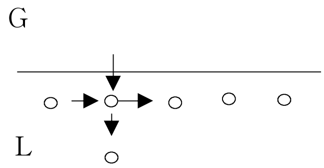
Chapter 4. Liquid-Gas and Liquid-Liquid Interface

surface 분자들은 안쪽으로 힘을 받는다.



• surface tension : 모든 물질이 구형이 되려는 성질

단위면적당 surface free energy $G^s=\gamma A$

surface 에 위치한 분자

⇒force unbalance에 의하여 힘을 inward 방향으로 받음.

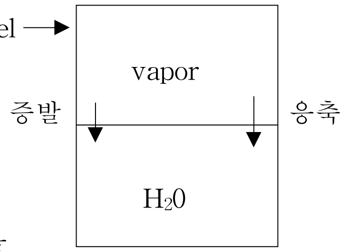
단위면적을 generation하는데 필요한 $E=\gamma$

γ(surface science ; surface에서 단위면적당 Gibbs free energy) ⇔ G (in bulk material)

γ의 단위 : energy per unit area (erg/cm^2)

$erg/cm^2=1dyn\cdot cm/cm^2=dyn/cm$=단위길이당 힘

• Turbulence in molecular level at surface



at equilibrium 증발속도=응축속도

1.2×10^{22} molecules/$cm^2\cdot$sec at 25℃ for H_2O

For H_2O 72.8dyn/cm=72.8erg/cm^2

For Hg 485dyn/cm=485erg/cm^2

surface energy(tension)이 매우 커서 drop → 모양 변화없음

• Surface science에서 알아야 할 것

- Laplace-Young Eq.
- Kelvin Eq.
- Gibbs Adsorption Eq.

① Laplace-Young Eq

work=$(\Delta P)(\Delta V)=(\Delta P)(4\pi r^2 dr)$

T, P등이 일정유지되면,

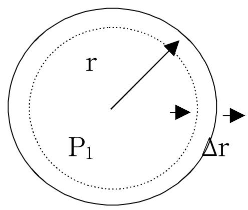
energy 변화량=$4\pi(r+dr)^2\cdot\gamma$[나중상태]$-4\pi r^2(r+dr)^2\cdot\gamma$[초기상태]

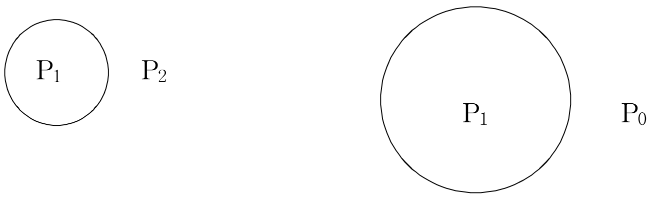
$=4\pi\gamma((r+dr)^2-r^2)$

$=4\pi\gamma(r^2+2rdr+(dr)^2-r^2)$

$=4\pi\gamma\cdot 2rdr=8\pi\gamma rdr=\Delta P4\pi r^2dr$

$\therefore \Delta P=2\gamma/r$ r이 작을수록 ΔP ↑ P_2





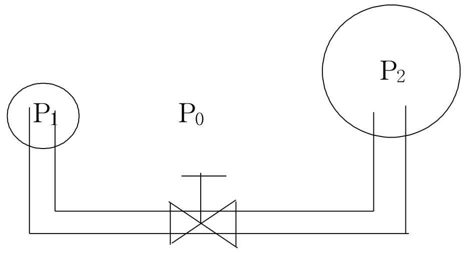
$P_2>P_1>P_0$

surface (viscosity) : g/cm N/m

bulk (〃) : g/cm-sec N/m^2

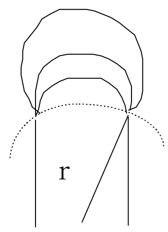
valve open → air flow 압력이 큰 P1에서 압력 작은 P2로 흐름

= 큰건 더 커지고 작은건 더 작아짐



$r_1<r_2$

$P_1>P_2>P_0$



hemi-sphere인 경우 ra minimum, 곡률반경이 점점 커진다.(=점점 plate해짐)

…small bubble의 곡률반경의 large bubble의 반경과 같아질때까지 air flow 진행

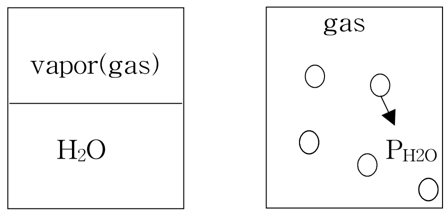
② Kelvin Eq.

P^{vap}_{H2O}=760mmHg at 100℃, 1atm

P^*_1 state 1에서 liquid와 평형을 이루고 있는 기상에서의 vapor pressure

P^*_2 state 2에서 liquid와 〃 〃 있는 기상에서의 vapor pressure

$dG_L=V_Ldp-S_LdT$=state2−state1$=G_{2,L}-G_{1,L}$



state 1 state 2

등온상태에서 적분

$\Delta G_L=\int_{state1}^{state2}V_Ldp=V_L\int_{P1}^{P2}dp=V\Delta P=\frac{2\gamma}{R}V$ $\Delta P=P^{inside}_{drop}-P_{bulk\ ligand}$

for liquid ⇒ V = constant

If vapor phase is ideal gas

$G=G^\circ+RT\ln P$ curve s

$G^*=G^\circ+RT\ln P^*$ plate s

$\Delta G=G^*-G=RT\ln\frac{P^*}{P}=\frac{2\gamma}{R}V$

100℃에서 끓는다 ⟶ 100℃보다 낮은 T에서 끓는다.

작게 분산시킴

내부압력 $\Delta P=P_1-P_0=\frac{2\gamma}{r}=\frac{2\times 73 dyn/cm}{10^{-9}m}=\frac{150 dyn/cm}{10^{-7}cm}=150\times10^7 dyn/cm^2$

$=150\times10^2 N/cm^2$

$=150\times10^6 N/m^2$

$G^1_L=G^1_G$ $G^2_L=G^2_G$

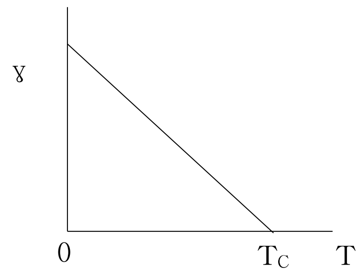
$\Delta G_L=G^2_L-G^1_L=G^2_G-G^1_G$

$=\{G^\circ_G+RT\ln P^*_2\}-\{G^\circ_G+RT\ln P^*_1\}=RT\ln\frac{P^*_2}{P^*_1}=V_L\frac{2\gamma}{R}$

- Variation of γ with temperature

γ↓ as T ↑ (surface tension 감소)

$\gamma[\frac{Mx}{P}]^{2/3}=k(Tc-T-b)$



• Variation of ɣ with pressure

in bulk $dG=Vdp-SdT$

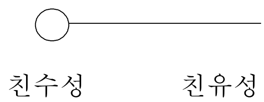
at surface $dG^s=V^s dp-S^s dT=d\gamma$

$(\frac{d\gamma}{dp})_T=V^S(+)$ $\therefore \gamma\uparrow$ as $P\downarrow$

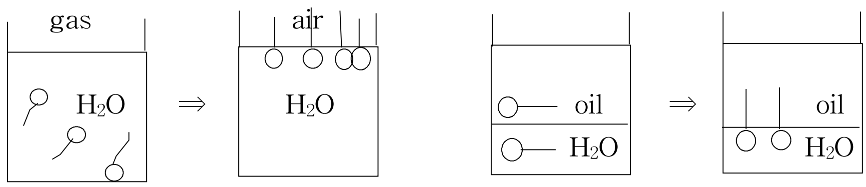
• surfactants(계면활성제) : surface active agent

계면(or 표면)에 흡착해서 계면(or 표면) 물성을 크게 변화시켜주는 물질

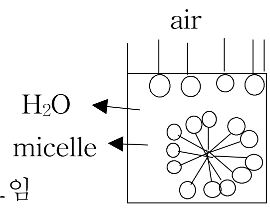
분자구조⇒한분자내에 친수성부분과 친유성부분이 동시에 존재하는 물질



ex) 지방산 + Glucose(설탕) ⟶ 지방산-Glucose



unstable



• surfactant의 특징

①표면물성 변화

②용액내에서 aggregate 형성

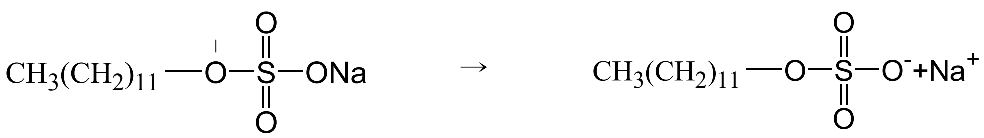
self-assembly oily if 벤젠등을 넣으면 이 부분에서 녹는다

크기:~100Å(투명하게 보임) 가시광선의 1/4이하면 투명하게 보임

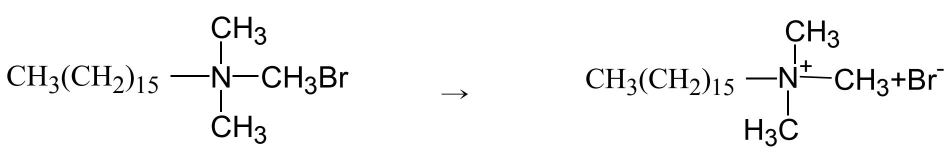
…물과 기름 섞어서 계면활성제에 쓰면 투명하게 보일수 있다.

• surfacant의 분류 : 수용액내에서 이온화되었을 때 surface active part의 ion종류에 따라 분류

①음이온성:수용액에 이온화되었을 때 surface active part가 음이온성

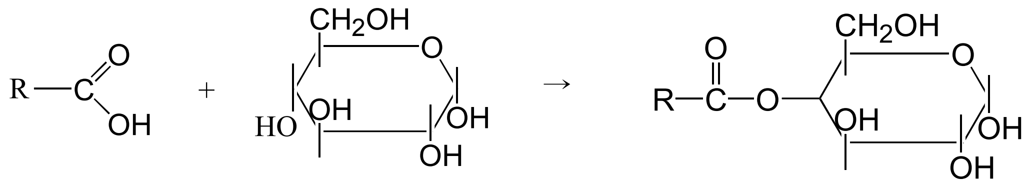


②양이온성:수용액에 이온화되었을 때 surface active part가 양이온성

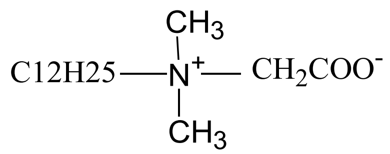


⇒ 헤어린스, 금속표면부식방지제

③비이온성:한분자내에 친수성과 친유성이 존재하나 수용액내에서 이온화되지 않는 surf.



④양쪽성:수용액의 ph에 따라 이온성이 변화되는 것

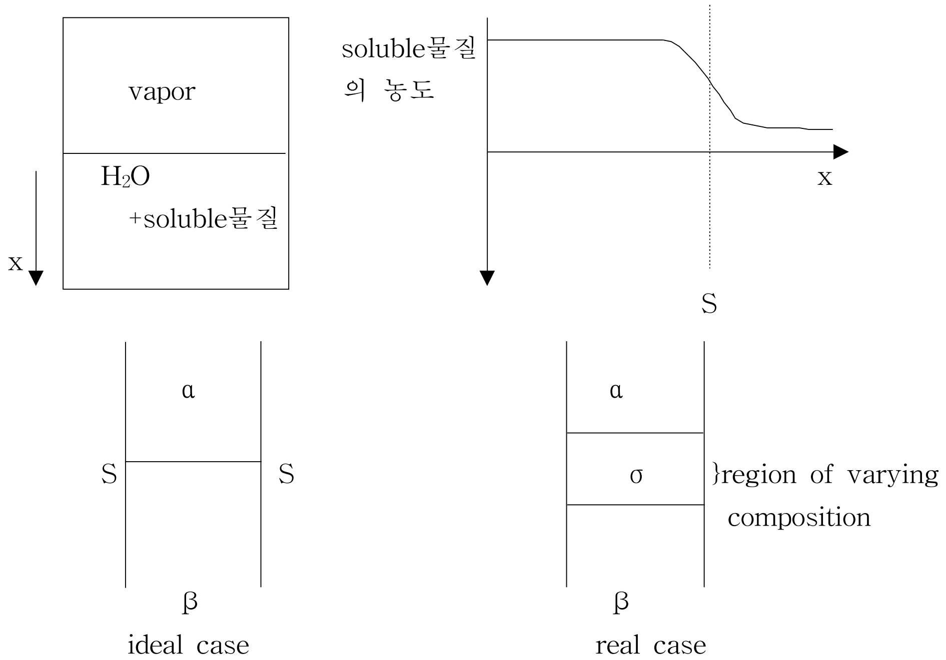


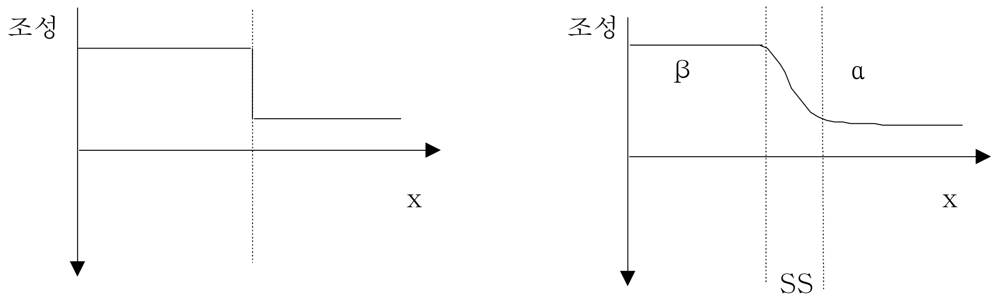
⇒ in acidic solution : cationic

in alkali solution : anionic

• Thermodynamics of adsorption

⇒ Gibbs adsorption equation for soluble material인 경우



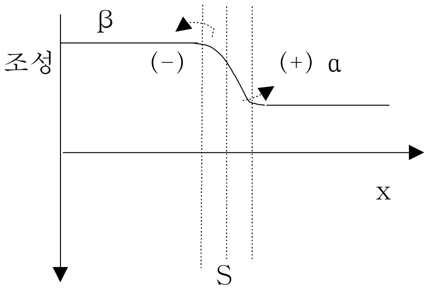


interface를 맘대로 정할수 있다

⇒물리적 조성등이 이후에 각각 정한거에 따라 결정됨

• surface excess concentration

n^{σ}_{i}:amount of component i in the interfacial phase σ in excess of that which would have been in σhad the bulk phase α and β extended to a surface ss with unchanging composition



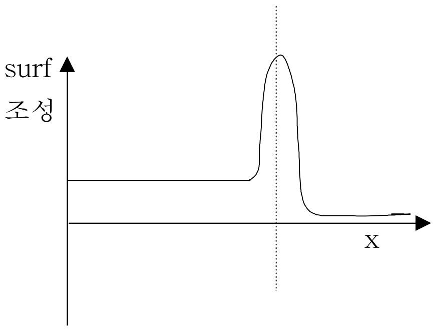
$n^{\sigma}_{i}=A-B$

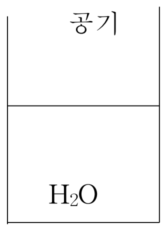
surface excess concentration

$\Gamma^{6}_{i}= n^{\sigma}_{i}/$(Iinterfial area)

: σphase (interfacial phase)에 존재하는 i성분의 양을 interfacial area로 나눈값

for surface active agent





Γ^{6}_{i} = positive

0 for a given system depending upon the position og ss

negative

• Internal Energy ⇒ for open bulk system

$U=TS-PV+\sum \mu_i n_i$

⇒ for open interfacial phase

$U=TS-PV+\gamma A+\sum \mu_i n_i$

$U^{\sigma}=TS^{\sigma}-PV^{\sigma}+\gamma A+\sum \mu_i n_i^{\sigma}$

at equilibrium $T^{\alpha}=T^{\beta}=T^{\sigma}=T$

$P^{\alpha}=P^{\beta}=P^{\sigma}=P$

$\mu_i^{\alpha}=\mu_i^{\beta}=\mu_i^{\sigma}=\mu_i$

미분하면 $du^{\sigma}=Tds^{\sigma}+S^{\sigma}dT-Pdv^{\sigma}-V^{\sigma}dp+\gamma dA+Ad\gamma+\sum \mu_i n_i^{\sigma}+\sum n_i d\mu_i$ ①

From the first law of thermodynamics (에너지보존 법칙)

⇒ $du^{\sigma}=Tds^{\sigma}-Pdv^{\sigma}+\gamma dA+\sum \mu_i n_i^{\sigma}$ ②

cf) $du=Tds-Pdv+\sum \mu_i\ dn_i+\gamma dA$

from eqn. ① & ②

①-② $S^{\sigma}dT-V^{\sigma}dp+Ad\gamma+\sum n_i^{\sigma}d\mu_i=0$

at constant T, P (dT=dp=0)

$Ad\gamma+\sum n_i^{\sigma}d\mu_i=0$ $\therefore d\gamma=\sum_i \frac{\mu_i^{\sigma}}{A}d\mu_i=-\sum \Gamma_i d\mu_i$

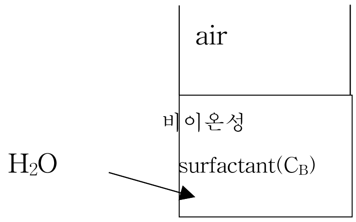
for binary system

$d\gamma = -\Gamma_A d\mu_A - \Gamma_B d\mu_B$

if, Γ_A=0이 되도록 driving surface를 선택하면

$d\gamma = -\Gamma_B d\mu_B$

그런데, $\mu_B = \mu_B^s + RT\ln a_B$ s:standard

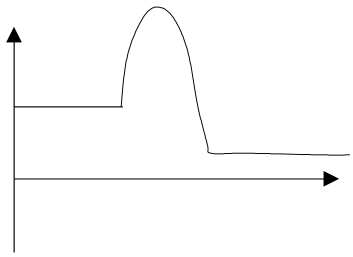


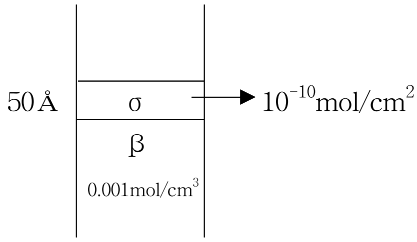
$d\mu_B = RT\ln a_B$

$d\gamma = -\Gamma_B RT d\ln a_B \quad \rightarrow \quad -\Gamma_B RT d\ln C_B \qquad \therefore \Gamma_B = -\frac{1}{RT}\frac{d\gamma}{d\ln C_B}$

$\Gamma_B = 10^{-10} mol/cm^2$ at surface ⇒ 이걸 2차원으로 바꾸면 C_B보다 1000배는 큼

$C_B = 0.001 mole/cm^3$ in bulk





for diluted binary system (i.e. non-ionic surfactant)

H_2O ⇒ A   non-ionic surfactant ⇒ B

$\Gamma_B = -\frac{1}{RT}\frac{d\gamma}{d\ln C_B}$

for diluted binary system (i.e. ionic surfactant)

$d\gamma = \Gamma_i d\mu_i$

$= \Gamma_A d\mu_A - \Gamma_B d\mu_B - \Gamma_C d\mu_C = -2\Gamma_B d\mu_B$

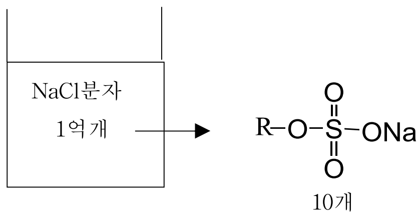
$\Gamma_B = \Gamma_C$ (electroneutrality condition) , $\mu_B = \mu_C$

$\mu^\circ_B + RTd\ln a_B = \mu^\circ_B + RTd\ln C_B$

$\mu^\circ_C + RTd\ln a_C = \mu^\circ_C + RTd\ln C_C \qquad \therefore \Gamma = -\frac{1}{2RT}\frac{d\gamma}{d\ln C_B}$

In the presence of excess electrolyte of ionic surfactant

$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln C_B}$



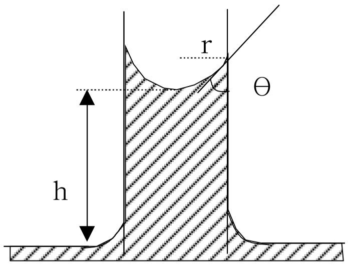
counterion이랑 같은 ion이 들어갈 때 $\Gamma_c d\mu_c = 0$

• Surfactant and Interfacial Tension의 측정법

①Capillary rise method

Capillary내 유체에서의 force balance.

중력=surface tension force



$\pi r^2 h\Delta\rho g = 2\pi r\gamma\cos\Theta$ $\Delta\rho=\rho_L-\rho_G$(부력)

$$\therefore \gamma = \frac{r\Delta\rho g h}{2\cos\Theta}$$

if, Θ=0 ⇒ complete wetting $r = \frac{r\Delta\rho g h}{2}$

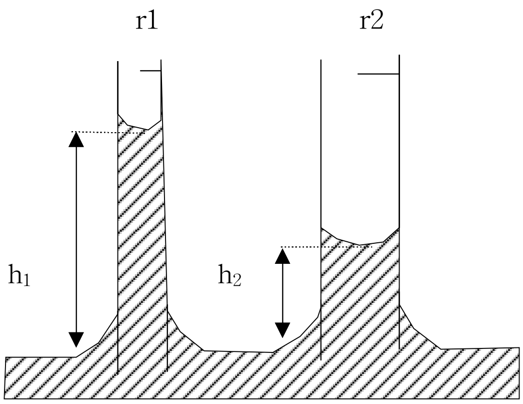
for hemi-spherical case

중력=surface tension force $\pi r^2 h\Delta\rho g + \{(\pi r2)\gamma\Delta\rho g - \frac{1}{2}\,\frac{4}{3}\pi r^3\Delta\rho g\}$

$$= \pi r^2 h\Delta\rho g + \frac{1}{3}\pi r^3\Delta\rho g = 2\pi r\gamma$$

$$\therefore \gamma = \frac{1}{2} r\left(h + \frac{\gamma}{3}\right)\Delta\rho g$$

using two capillary tube



$$\gamma = \frac{1}{2} r_1 h_1 \Delta\rho g = \frac{1}{2} r_2 h_2 \Delta\rho g$$

$$h_1 = \frac{\gamma}{\frac{r_1\Delta\rho g}{2}}, \quad h_2 = \frac{\gamma}{\frac{r_2\Delta\rho g}{2}}$$

$$\Delta h = h_1 - h_2 = 2\gamma \frac{1}{\Delta\rho g}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$

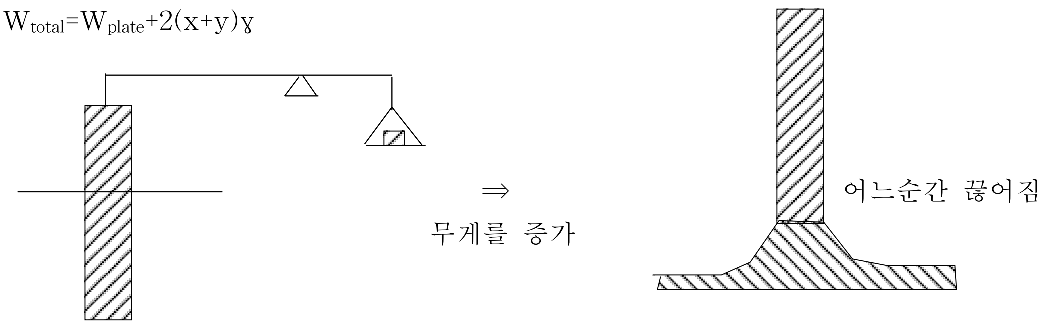
$$\therefore \gamma = \frac{\Delta\rho g\, r_1 r_2 \Delta h}{2(r_2 - r_1)}$$

if complete wetting ⇒ cosΘ무시 ; 재질과 액체가 같으면 cosΘ도 같다

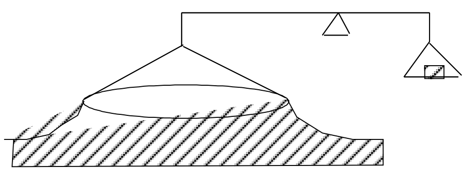
wetting agent ⇒ 계면활성제가 들어가면 Θ=0이 된다. ⇒ cosΘ=1로 무시

②Wilhelmy Plate method

$W_{total} = W_{plate} + 2(x+y)\gamma$



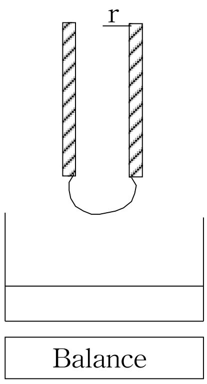
③Ring Method



어느순간되면 떨어진다.

$F = 2(2\pi R)\gamma$(∵링의 안쪽과 바깥에서 힘받으므로)

④Drop weight method



i)non-wetting mg(drop 1개의 무게)=2πrɣ

$ɣ = \frac{\Phi mg}{2\pi r}$ (Φ:correction facter Fig.4-8)

이 경우 error가 많다 ⇒the drop does not leave completely tip

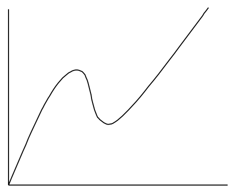
⇒surface tension is not exactly vertical

ex)teflon, wax

:일정방울을 떨어뜨리고 늘어난 무게만큼 divide ⇒ 1drop무게

ii)wetting

mg=2πr′ɣ $ɣ = \frac{\Phi mg}{2\pi r'}$ Φ

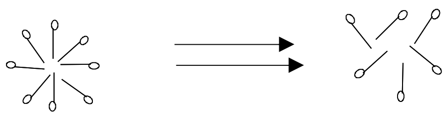


r/$V^{1/3}$

V:drop 1개의 volume

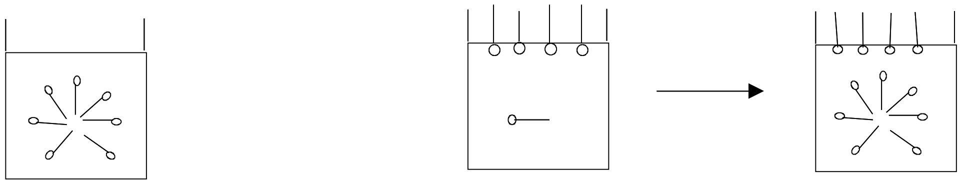
r :tube의 반경

• Association Colloid



(monomer상태)

statistical characteristic(통계적)

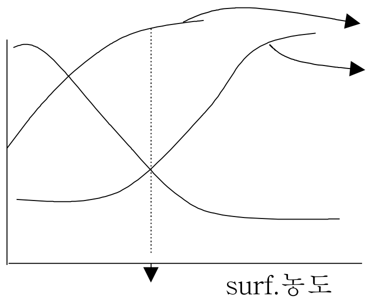


discrete H$_2$O 친유성 part는 H$_2$O로부터 squeeze out

(at low concentration) (at high concentration)

inflection point

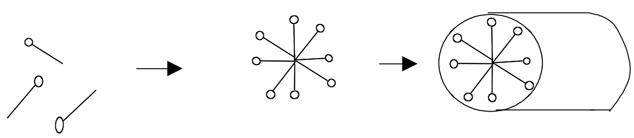
물성



전기전도도

가용화력

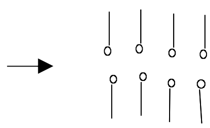
surf.농도



monomer spherical cylinderical

CMC(critical micelle concentration)

⇒눈에 보이지는 않지만 microstructure됨



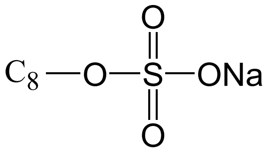
LC

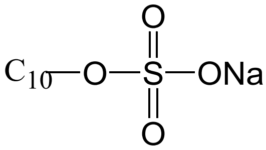
cf)Theory Jounal of American oil chemists Sociaty

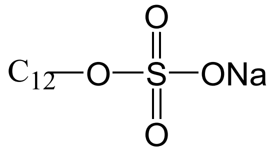
nano tube ⇒ H_2 gas 저장

• Factors affecting critical micelle concentration

① CMC ↓ as H.C(hydro carbon)의 길이↑(H.C길이↑ 더 낮은 농도에서 spherical 형성)





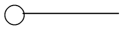


128mM　　　　　　　　　　　　　　　　　　8.0mM

ion성 : 각 탄소길이마다 1/2씩 CMC↓

non-ion성 :　〃　1/3　〃

② CMC↑ as T↑



친수성　친유성⇒micelle의 driving force

③ oraganic molecules

urea(water structure breaker)⇒CMC↑

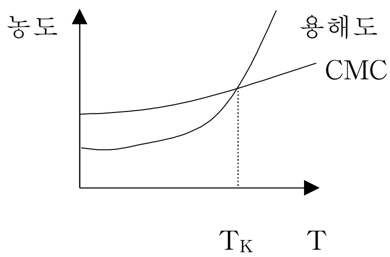
Fructose, Maltose(water structure promotor)⇒CMC↓

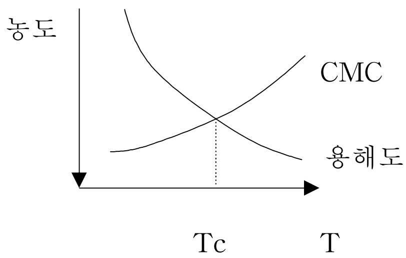
• micelle구조

monomer → spherical → cylinderical → lamellar

• solublization : water-insoluble 물질이 수용액내에 존재하는 micelle내부로 녹아들어가는 현상

• Krafft point (for only ionic surf)　　　　Clouding point (for only nonionic surf)





: T_K이하에선 micelle 형성안됨

: Tc이상에서 micelle 형성안됨

비이온계면활성제는 T↑,용해도↓

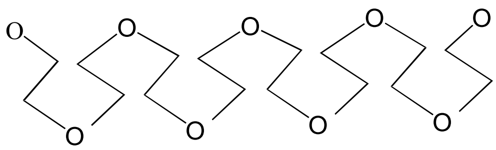
T↓ chain이 압축되어있어 O가 물과 접촉해서 용해

T↑ chain이 펴져서 용해↓

$-(OCH_2CH_2CH_2)_n-$ 친유성

$-(OCH_2CH_2)_n-$ 친수성

$-(OCH_2)_n-$ 친유성



• work of adhesion : 다른 종류 column ⇒ $W_{adhesion}=\gamma_A+\gamma_B-\gamma_{AB}$

work of cohesion : 같은 종류 column ⇒ $W_{adhesion}=\gamma_A+\gamma_B-\gamma_{AB}$ 0