Brief introduction to liquid surfaces & liquid/liquid interfaces,
Special open lectures on "Selected Topics in Physical Chemistry of Interface".
Department of Electronic Chemistry, Titech
Summer 2007,
distributed by Hyuk Yu
June 20, 2007

References:

1. **"Physics & Chemistry of Interfaces", Hans-Jürgen Butt, Karlheinz Graf & Michael Kappl, 2003, Wiley-VCH.**
2. **"Physical Chemistry of Surfaces", Arthur W. Adamson & Alice P. Gast, 1997, Wiley.**
3. **"Principles of Colloid & Surface Chemistry", 2nd edition, Paul C. Hiemenz, 1986, Dekker.**
4. **"Introduction to Colloid and Surface Chemistry, 4th edition", Duncan J. Shaw, 1992, Butterworth-Heinemann.**
5. **"Capillarity & Wetting Phenomena", P-G de Gennes, F. Brochard-Wyart, D. Quere, 2004, Springer**

Continuation of lectures started on June 19, 2007

6. Additivity of intermolecular forces at interface; interfacial tension of immiscible liquids from their surface tensions.

7. Thermodynamics of adsorption & Gibbs adsorption isotherm.

8. Critical micelle concentration, cmc, of surfactants.

9. Monomolecular layers and their structure & dynamics.

6. Additivity of intermolecular forces at interface; interfacial tension of immiscible liquids from their surface tensions.

The additivity rules and Girifalco-good-Fowkes equation.

$\gamma_{AB} = \gamma_A + \gamma_B - 2\sqrt{\gamma_A^d \gamma_B^d}$, a semi-empirical formula that relies on the dispersion interaction component of surface tension.

The additivity rules are based on the following assumptions:

1. surface tension of water consists of the dispersion & hydrogen bonding interactions.
   $\gamma_W = \gamma_W^d + \gamma_W^h$
2. surface tension of mercury consists of the dispersion & metallic interactions
   $\gamma_{Hg} = \gamma_{Hg}^d + \gamma_{Hg}^m$
3. surface tension of hydrocarbon arises mainly from the dispersion interactions.
   $\gamma_{HC} = \gamma_{HC}^d$

Four broad categories of molecular interactions

1. **Hydrogen bonding: Hydrogen atoms serve as bridges linking together two atoms of high electronegativity. In the present context these atoms are in separate molecules so the molecules themselves are mutually "attracted" by these bonds.**
2. **Metallic bonding: A sea of mobile electrons shared by the atoms of a metal contributes to the attraction between metal atoms in bulk samples.**
3. **Permanent dipole interactions: Polar molecules have relatively positive and negative regions. Regions of opposite charge on different molecules result in an attraction between these molecules. Molecules must possess a permanent dipole moment to display this effect.**
4. **London forces: Deformable electron clouds in adjoining molecules distort one another, resulting in an instantaneous polarity with accompanying attraction between the molecules involved. The polarizability of a molecule (see Sect. 5.3) is a measure of its tendency to display this effect.**

Examples: All values are in units of mN/m at 20°C.

$\gamma_{Hg} = 484$

$\gamma_{hexane} = 18.4$ $\quad$ interfacial tension $\quad$ $\gamma_{hexane/Hg} = 378$

$\gamma_{octane} = 21.8$ $\quad$ $\gamma_{octane/Hg} = 375$

$\gamma_{benzene} = 28.9$ $\quad$ $\gamma_{benzene/Hg} = 363$

Thus $\gamma_{Hg}^d = \left(\frac{484 + 18.4 - 378}{2}\right)^2 \cdot \frac{1}{18.4} = 210$ from hexane

$\gamma_{Hg}^d = \left(\frac{484 + 21.8 - 375}{2}\right)^2 \cdot \frac{1}{21.8} = 196$ from octane

$\gamma_{Hg}^d = \left(\frac{484 + 28.9 - 363}{2}\right)^2 \cdot \frac{1}{28.9} = 195$ from benzene

Ave 200 ± 10

So, $\gamma_{toluene/Hg} = 484 + 28.5 - 2(200 \cdot 28.5)^{1/2} = 362$ deduced

359 exptl determined

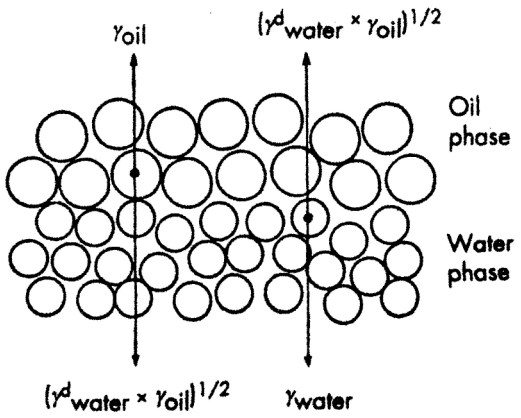


Figure 4.2 Schematic representation of the contributions to an oil–water interfacial tension

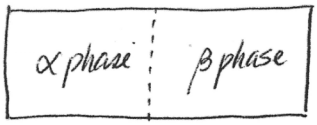
Table 6.4 Experimental Values for γ_H, γ_{H-W}, and γ_{H-Hg}, With H = Hydrocarbon, at 20°C (all values in mJ m^{-2})[a]

		Mercury (γ_{Hg} = 484)		Water (γ_W = 72.8)	
Hydrocarbon	γ	γ_{H-Hg}	γ^d_{Hg}	γ_{H-W}	γ^d_W
n-Hexane	18.4	378	210	51.1	21.8
n-Heptane	18.4	—	—	50.2	22.6
n-Octane	21.8	375	199	50.8	22.0
n-Nonane	22.8	372	199	—	—
n-Decane	23.9	—	—	51.2	21.6
n-Tetradecane	25.6	—	—	52.2	20.8
Cyclohexane	25.5	—	—	50.2	22.7
Decalin	29.9	—	—	51.4	22.0
Benzene	28.85	363	194	—	—
Toluene	28.5	359	208	—	—
o-Xylene	30.1	359	200	—	—
m-Xylene	28.9	357	211	—	—
p-Xylene	28.4	361	203	—	—
n-Propylbenzene	29.0	363	194	—	—
n-Butylbenzene	29.2	363	193	—	—
Average			200±7		21.8±0.7

[a]Here γ^d_{Hg} and γ^d_W are calculated as in Example 6.6.
Source: Data from F. M. Fowkes, *Ind. Eng. Chem., 56*:40 (1964).

7. Thermodynamics of adsorption & Gibbs adsorption isotherm

Ideal Gibbs Interface:



interfacial plane

$V = V^\alpha + V^\beta$
$U = U^\alpha + U^\beta + U^\sigma$
$n_i = n_i^\alpha + n_i^\beta + n_i^\sigma$
$S = S^\alpha + S^\beta + S^\sigma$

U^α: internal energy per unit vol
c_i^α: conc of i^{th} species in α-phase

$\therefore U^\sigma = U - u^\alpha V^\alpha - u^\beta V^\beta$

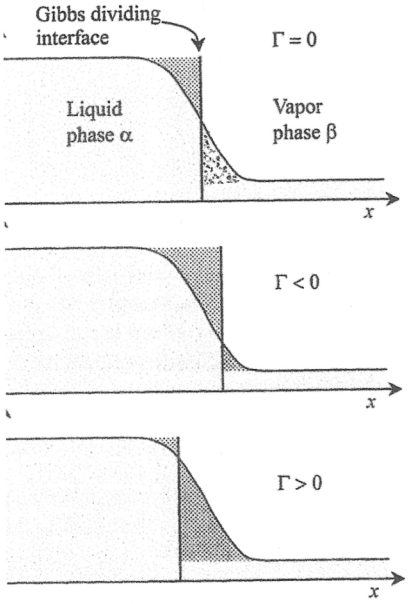
$n_i^\sigma = n_i - c_i^\alpha V^\alpha - c_i^\beta V^\beta$

Interfacial excess of i^{th} species, $\Gamma_i \equiv \frac{n_i^\sigma}{A}$

Position dependence for liquid-vapor interface of pure system

$n^\sigma = n - c^\alpha V^\alpha - c^\beta V^\beta$

$\Gamma = 0, \quad n = c^\alpha V^\alpha + c^\beta V^\beta$
$\Gamma < 0, \quad n < c^\alpha V^\alpha + c^\beta V^\beta$
$\Gamma > 0, \quad n > c^\alpha V^\alpha + c^\beta V^\beta$



Dependence of the surface excess Γ on the position of the Gibbs dividing plane

Interface excesses in multi-component systems

Let "1" be designated for solvent, & note that $V^\alpha = V - V^\beta$

$$n_i^\sigma = n_i - C_i^\alpha V^\alpha - C_i^\beta V^\beta = n_i - C_i^\alpha (V - V^\beta) - C_i^\beta V^\beta$$
$$= n_i - C_i^\alpha V + (C_i^\alpha - C_i^\beta) V^\beta$$

All quantities in RHS of this equation are invariant with the position of interfacial plane except V^β

Similarly $n_i^\sigma = n_i - C_i^\alpha V + (C_i^\alpha - C_i^\beta) V^\beta$

$$\rightarrow n_1^\sigma \frac{(C_i^\alpha - C_i^\beta)}{(C_1^\alpha - C_1^\beta)} = (n_1 - C_1^\alpha V) \frac{(C_i^\alpha - C_i^\beta)}{(C_1^\alpha - C_1^\beta)} + (C_i^\alpha - C_i^\beta) V^\beta$$

Eliminating V^β,

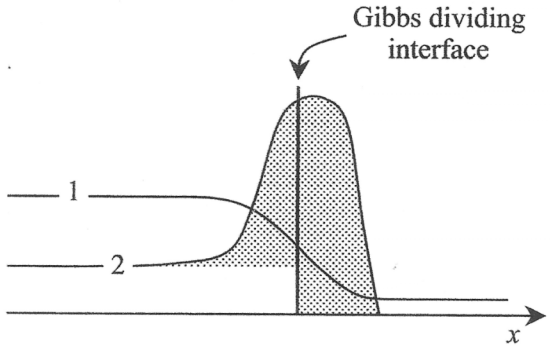
$$n_i^\sigma - n_1^\sigma \cdot \frac{(C_i^\alpha - C_i^\beta)}{(C_1^\alpha - C_1^\beta)} = (n_i - C_i^\alpha V) - (n_1 - C_1^\alpha V) \left(\frac{C_i^\alpha - C_i^\beta}{C_1^\alpha - C_1^\beta} \right)$$

All quantities in RHS are indept of the position of interfacial plane, hence LHS must all be indept of the position.

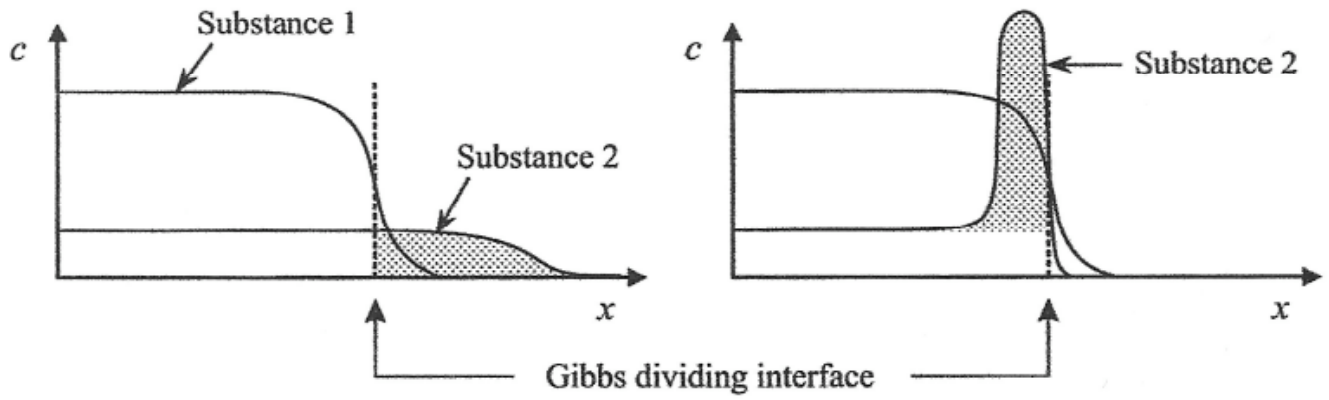
Dividing by A of LHS

$$\Gamma_i^{(1)} \equiv \Gamma_i - \Gamma_1 \left(\frac{C_i^\alpha - C_i^\beta}{C_1^\alpha - C_1^\beta} \right),$$ relative adsorption of i^{th} species with respect to 1, which is indept of the position of plane, so we choose it to be such that $\Gamma_1 = 0$

$$\Gamma_i^{(1)} = \Gamma_i \quad (\Gamma_1 = 0)$$



Concentration profile of a solute (2) dissolved in a solvent (1). The area of the dotted region corresponds to the surface excess $\Gamma_2^{(1)}$ (Γ_1=0).



Examples of two different concentration profiles giving rise to the same interfacial excess concentration, $\Gamma_2^{(1)}$.

Basic thermodynamics of Interface.

State with internal energy since its variation contains all extensive properties

- $dU = TdS - PdV + \sum \mu_i dn_i + dW$

$= dU^\alpha + dU^\beta + dU^\sigma$

$= TdS - P^\alpha dV - (P^\beta - P^\alpha) dV^\beta + \sum \mu_i^\alpha dn_i^\alpha + \sum \mu_i^\beta dn_i^\beta + \sum \mu_i^\sigma dn_i^\sigma + \gamma dA$

$dV = dV^\alpha + dV^\beta$, $\because dV^\sigma = 0$, $dV^\alpha = dV - dV^\beta$

- Helmholtz free energy F (instead of A to avoid confusion with area A)

$dF = -SdT - PdV + \sum \mu_i dn_i + dW$

$= -SdT - P^\alpha dV - (P^\beta - P^\alpha) dV^\beta + \sum \mu_i^\alpha dn_i^\alpha + \sum \mu_i^\beta dn_i^\beta + \sum \mu_i^\sigma dn_i^\sigma + \gamma dA$

At const T & V,

$dF = -(P^\beta - P^\alpha) dV^\beta + \sum \mu_i^\alpha dn_i^\alpha + (\beta) + (\sigma) + \gamma dA$

At equilibrium, $\mu_i^\alpha = \mu_i^\beta = \mu_i^\sigma$ for a closed system

Proof: $dn_i = 0$, $n_i = n_i^\alpha + n_i^\beta + n_i^\sigma$, $dn_i^\sigma = -dn_i^\alpha - dn_i^\beta$

$dF = -(P^\beta - P^\alpha) dV^\beta + \sum (\mu_i^\alpha - \mu_i^\sigma) dn_i^\alpha + \sum (\mu_i^\beta - \mu_i^\sigma) dn_i^\beta + \gamma dA$

Under T, V, n_i const, F is minimized,

$\frac{dF}{dn_i^\alpha} = 0$, $\frac{dF}{dn_i^\beta} = 0$

$\hookrightarrow \mu_i^\alpha = \mu_i^\sigma$ $\hookrightarrow \mu_i^\beta = \mu_i^\sigma$, QED

At equilibrium with T, V, n_i const.

$$dF = -(P^\beta - P^\alpha)dV^\beta + \sum \mu_i dn_i + \gamma dA$$

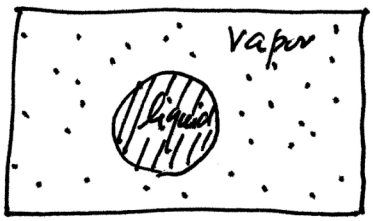
Hence, $\left(\frac{\partial F}{\partial A}\right)_{n_i, T, V, V^\beta} = \gamma$, phase volumes must also be const, $dV^\alpha + dV^\beta = 0$

Note that V^β & A are related, so that both cannot vary independently.

Location of Interface

Interfacial tension depends on the location of Gibbs dividing plane for curved surface, but it does not for flate surface.

Example:



α: vapor phase
β: liquid phase

$V^\beta = \frac{4\pi}{3} r^3$, $A = 4\pi r^2$

$= \frac{4\pi}{3}\left(\frac{A}{4\pi}\right)^{3/2}$

So, $\frac{\partial V^\beta}{\partial A} = \frac{r}{2}$, $P^\beta - P^\alpha = \frac{2\gamma}{r}$

If the interface is at r', then $P^\beta - P^\alpha = \frac{2\gamma'}{r'}$

$\gamma \neq \gamma'$ if $r \neq r'$

In general $\frac{\partial V^\beta}{\partial A} = \frac{1}{\frac{1}{R_1} + \frac{1}{R_2}}$,

Hence, $P^\beta - P^\alpha = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$, Young-Laplace Equ recovered!

Other thermodynamic quantities:

Consider an open system with surface work in addition to the P-V work.

$$dU = TdS - PdV + \sum \mu_i dn_i + \gamma dA$$
$$dH = TdS + VdP + \sum \mu_i dn_i + \gamma dA$$
$$dG = -SdT + VdP + \sum \mu_i dn_i + \gamma dA, \quad \gamma \equiv \left(\frac{\partial G}{\partial A}\right)_{T,P,n_i}$$
$$dF = -SdT - PdV + \sum \mu_i dn_i + \gamma dA, \quad \gamma \equiv \left(\frac{\partial F}{\partial A}\right)_{T,V,n_i}$$

(Closed system)

Consider only the interface components,

$$dU^\sigma = TdS^\sigma + \sum \mu_i dn_i^\sigma + \gamma dA, \quad \because V^\sigma = 0,\ dV^\sigma = 0$$

Integrating, $U^\sigma = TS^\sigma + \sum \mu_i n_i^\sigma + \gamma A$

$$H^\sigma = U^\sigma - \gamma A, \because PV^\sigma = 0, \quad \because H^\sigma = U^\sigma - \underbrace{(\gamma A - PV^\sigma)}_{\text{total mechanical work}}$$

$$G^\sigma = H^\sigma - TS^\sigma = \sum \mu_i n_i^\sigma$$
$$F^\sigma = U^\sigma - TS^\sigma = \sum \mu_i n_i^\sigma + \gamma A,$$

Hence, $G^\sigma/A = \sum \mu_i \left(\frac{n_i^\sigma}{A}\right) + \gamma = \sum \mu_i \Gamma_i$

$$F^\sigma/A = \sum \mu_i \Gamma_i + \gamma$$

Differentiation of F^σ, $dF^\sigma = dU^\sigma - TdS^\sigma - S^\sigma dT$

$$= TdS^\sigma + \sum \mu_i dn_i^\sigma + \gamma dA - TdS^\sigma - S^\sigma dT$$
$$= -S^\sigma dT + \sum \mu_i dn_i^\sigma + \gamma dA$$

Under $n_i^\sigma = \text{const}$,

a Maxwell's relationship arises to relate T-depd of γ to S^σ,

$$-\left(\frac{\partial S^\sigma}{\partial A}\right)_{n_i^\sigma, T} = \left(\frac{\partial \gamma}{\partial T}\right)_{n_i^\sigma, A}$$

Differentiation of H^σ

$$dH^\sigma = dU^\sigma - \gamma dA - Ad\gamma = TdS^\sigma + \sum \mu_i dn_i^\sigma - Ad\gamma$$

For pure liquids, $n^\sigma = 0$, Gibbs dividing plane is chosen to make $n^\sigma = 0$

Then, $dU^\sigma = TdS^\sigma + \gamma dA$, integrating $U^\sigma = TS^\sigma + \gamma A$

$$u^\sigma \equiv U^\sigma/A = Ts^\sigma + \gamma = \boxed{\gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_{A,P}}, \quad \left(\frac{\partial S^\sigma}{\partial A}\right)_T = \left(\frac{\partial \gamma}{\partial T}\right)_A$$

measurable

$$dF^\sigma = -S^\sigma dT + \gamma dA + \sum \mu dn^\sigma$$

$$\frac{F^\sigma}{A} = \gamma, \quad \boxed{f^\sigma = \gamma}$$

$$\boxed{s^\sigma = -\left(\frac{\partial \gamma}{\partial T}\right)_{A,P}}$$

Example: Water at 25°C, γ = 74.23 mN/m at 10°C, 71.99 mN/m at 25°C, 67.94 mN/m at 50°C

f^σ, s^σ, u^σ at 25°C

$f^\sigma = 71.99$ mN/m

$$s^\sigma = -\left(\frac{\partial \gamma}{\partial T}\right)_{A,P} = +\left(\frac{6.29}{40}\right)\cdot 10^{-3}\ \text{N/m·K} = +1.57\cdot 10^{-4}\ \text{N/m·K}$$

$$u^\sigma = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_{A,P} = 71.99\cdot 10^{-3} + 298\cdot 1.57\cdot 10^{-4} = 118.8\ \text{mN/m}$$

- Heat absorbed in a reversible increase in A

$$q\,dA = \delta Q = TdS = Ts^\sigma dA = -T\left(\frac{\partial \gamma}{\partial T}\right)_{P,A}\cdot dA$$

$$q = -T\left(\frac{\partial \gamma}{\partial T}\right)_{P,A} = 46.8\ \text{mJ/m}^2$$ – heat absorbed by expanding A

$$\gamma = u^{\sigma} - Ts^{\sigma}$$

$$s^{\sigma} = -\left(\frac{\partial \gamma}{\partial T}\right)_{P,A}, \quad u^{\sigma} = \gamma - T \cdot \left(\frac{\partial \gamma}{\partial T}\right)_{P,A}$$

Table 3.1: Surface tension, surface entropy, surface enthalpy, and internal surface energy of some liquids at 25°C.

	$\gamma = f^{\sigma}(\mathrm{mNm}^{-1})$	$T \cdot s^{\sigma}(\mathrm{mNm}^{-1})$	$u^{\sigma}(\mathrm{mNm}^{-1})$
Mercury	485.48	61.1	549.6
Water	71.99	46.9	121.1
n-hexane	17.89	30.5	49.9
n-heptane	19.65	29.2	50.3
n-octane	21.14	28.3	50.9
n-nonane	22.38	27.9	51.7
n-decane	23.37	27.4	52.2
Methanol	22.07	23.0	46.3
Ethanol	21.97	24.8	48.0
1-propanol	23.32	23.1	47.6
1-butanol	24.93	26.8	53.0
1-hexanol	23.81	29.8	55.6
Toluene	27.93	35.4	65.1

Gibbs Adsorption Isotherm

$$d\gamma = -\sum \Gamma_i d\mu_i$$

For binary systems, $d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$

or $d\gamma = -\Gamma_2^{(1)} d\mu_2 \quad (\Gamma_1 = 0)$

$$\Gamma_2^{(1)} = -\frac{a_2}{RT}\left(\frac{\partial \gamma}{\partial a_2}\right)_T = -\frac{c_2}{RT}\left(\frac{\partial \gamma}{\partial c_2}\right)_T$$

$a_2 = c_2$ (dilute sol'n)

Derivation:

$$U^\sigma = TS^\sigma + \sum \mu_i n_i^\sigma + \gamma A$$

$$dU^\sigma = T dS^\sigma + S^\sigma dT + \sum \mu_i dn_i^\sigma + \sum n_i^\sigma d\mu_i + \gamma dA + A d\gamma$$

also, $dU^\sigma = T dS^\sigma - P dV^\sigma + \sum \mu_i dn_i^\sigma + \gamma dA$

Combining the two, $S^\sigma dT + \sum n_i^\sigma d\mu_i + A d\gamma = 0$

T const, $A d\gamma = -\sum n_i^\sigma d\mu_i$,

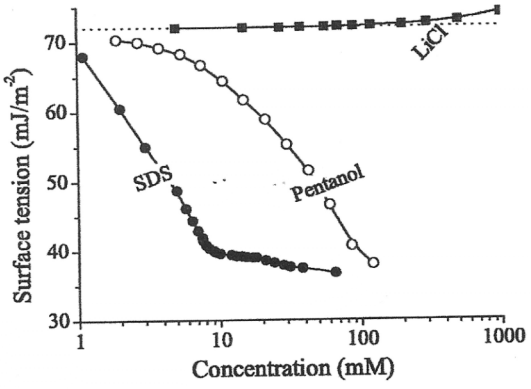
or $d\gamma = -\sum \Gamma_i d\mu_i$

For binary, $d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$

$\mu_2 = \mu_2^\circ + RT \ln a_2$, $d\mu_2 = RT\, d\ln a_2 = \frac{RT}{a_2} da_2$

$\therefore d\gamma = -\Gamma_2^{(1)} \frac{RT}{a_2} da_2 \quad (T = \text{Const})$

$$\boxed{\Gamma_2^{(1)} = -\frac{a_2}{RT}\left(\frac{\partial \gamma}{\partial a_2}\right)_T}$$



Solute	$d(\Delta\gamma)/dc(10^{-3}\,\mathrm{Nm^{-1}M^{-1}})$
HCl	−0.28
LiCl	1.81
NaCl	1.82
CsCl	1.54
CH_3COOH	−38

Table 3.2: Gradient of the adsorption isotherm for $c \to 0$ of different solutes in water at 25°C.

Example: SDS solution in water at 25°C

$\gamma(0) = 71.99\ \mathrm{mN/m}$, $\gamma(0.5\,\mathrm{mM}) = 69.09\ \mathrm{mN/m}$

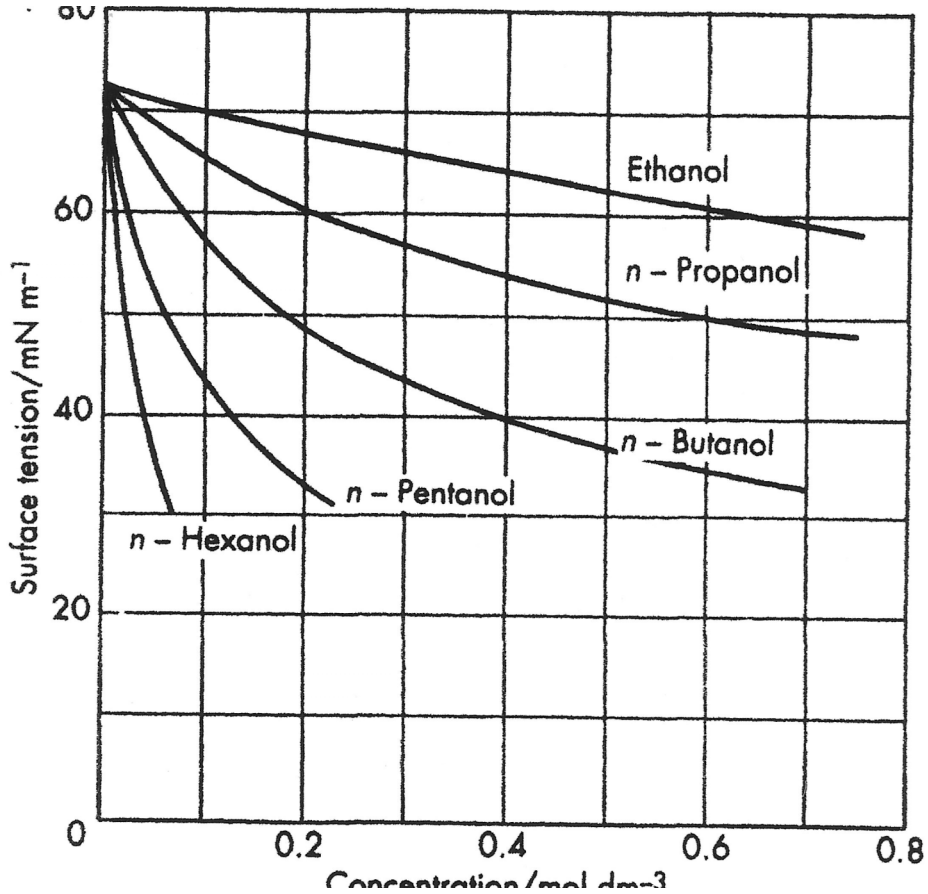
$$\lim_{C_2 \to 0}\left(\frac{\partial\gamma}{\partial C_2}\right)_T = \left(\frac{\Delta\gamma}{\Delta C_2}\right)_T = -\frac{2.90\cdot10^{-3}\ \mathrm{J/m^2}}{0.5\ \mathrm{mol/m^3}} = -5.80\ \frac{\mathrm{mN\cdot m^2}}{\mathrm{mol}}$$

$$\Gamma_2 = \frac{-0.5\ \mathrm{mol/m^3}}{8.31\cdot298\ \frac{\mathrm{J}}{\mathrm{mol}}}\cdot\left(-5.80\cdot10^{-3}\ \frac{\mathrm{J\cdot m}}{\mathrm{mol}}\right) = 1.17\cdot10^{-6}\ \frac{\mathrm{mol}}{\mathrm{m^2}}$$

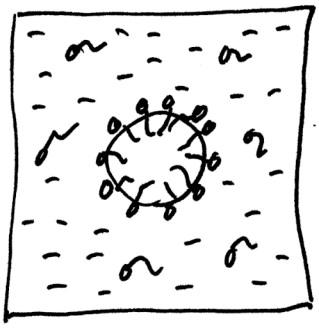
$$A_2 = \frac{1}{\Gamma_2} = \frac{10^6\ \mathrm{m^2}}{1.17\cdot6.02\cdot10^{23}\ \mathrm{molecule}} = 1.42\cdot10^{-18}\ \frac{\mathrm{m^2}}{\mathrm{molec}} = 1.42\ \frac{\mathrm{nm^2}}{\mathrm{molec}}$$

$$= 142\,\mathrm{Å^2/molec} \cong (12\,\mathrm{Å})^2/\mathrm{molec}$$

assuming the molecules are adsorbed in a monolayer.



Example: An air bubble with a radius of 1 cm is stabilized by SDS molecules in 2 mM solution in water at 25°C. It is given that a SDS molecule occupies 0.7 nm²/molecule on the interface. What is the pressure difference across the interface in 2 mM SDS solution? How about the pressure difference in pure water?



- Determine γ for the SDS covered interface. Then

$$\Delta P = \frac{2\gamma}{r}$$

$A_2 = 0.7\,nm^2/molecule$, $\Gamma_2 = \dfrac{1}{6.022\cdot10^{23}\,molecule/mole \cdot 0.7\cdot10^{-18}\,m^2/molecule} = 2.37\cdot10^{-6}\,\dfrac{mol}{m^2}$

$$\Gamma_2 = -\frac{C_2}{RT}\frac{\Delta\gamma}{\Delta C_2} = \frac{2\,mol/m^3}{2.48\cdot10^3\,J/mol}\cdot\frac{(71.99-\chi)\cdot10^{-3}\,J/m^2}{2\,mol/m^3} = 2.37\cdot10^{-6}\,\frac{mol}{m^2}$$

$$(71.99-\chi)\,10^{-6} = 2.37\cdot2.48\cdot10^{-6},\quad \chi = 71.99-5.90$$

$$= 66.09\cdot mN/m$$

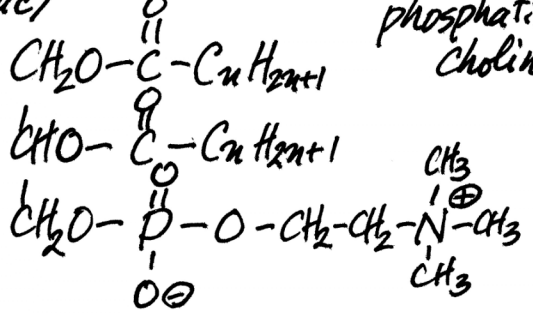
$$\Delta P = \frac{2\cdot66.1\cdot10^{-3}\,J/m^2}{10^{-2}\,m} = 13.2\,N/m^2$$

$$= 13.2\,Pa$$

In pure water, $\Delta P = \dfrac{2\cdot71.99\cdot10^{-3}}{10^{-2}} = 14.4\,Pa$

9. Critical micelle concentration, cmc, of surfactants.

Surfactants (surface active agents), amphiphiles, are commonly used terms to designate a class of molecules consisting of hydrophilic & hydrophobic parts.

Classification	Example
o Anionic	$C_{12}H_{25}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{\ominus}\ Na^{\oplus}$ sodium dodecyl sulfate (SDS) $C_{15}H_{31}COO^{\ominus}\ Na^{\oplus}$ a fatty acid sodium salt (SOAP)
o Cationic	$C_{12}H_{25}-\overset{\overset{CH_3}{\|}}{\underset{\underset{CH_3}{\|}}{N^{\oplus}}}-CH_3\ Br^{\ominus}$ hexadecyl trimethyl ammonium bromide or cetyl trimethyl ammonium bromide (CTAB)
o Nonionic	C_nE_m, $C_{10}E_8 = C_{10}H_{21}(OCH_2CH_2)_8OH$ alkyl ethylene glycol   alkyl glucoside
o Amphoteric (or Zwitterionic)	

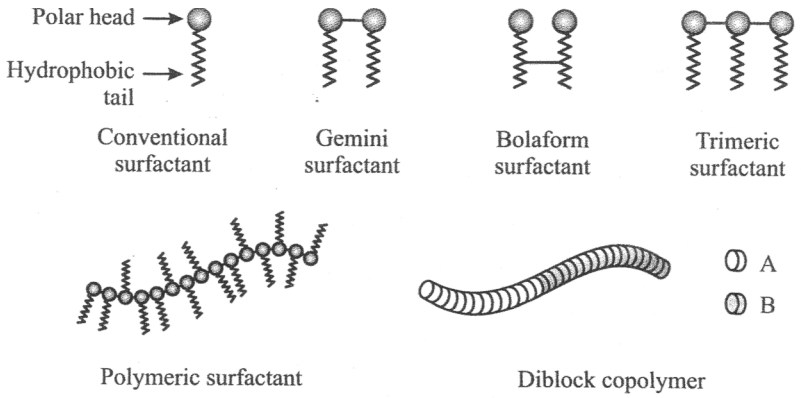
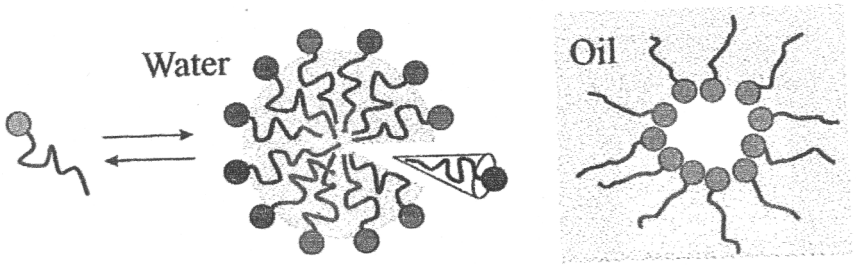
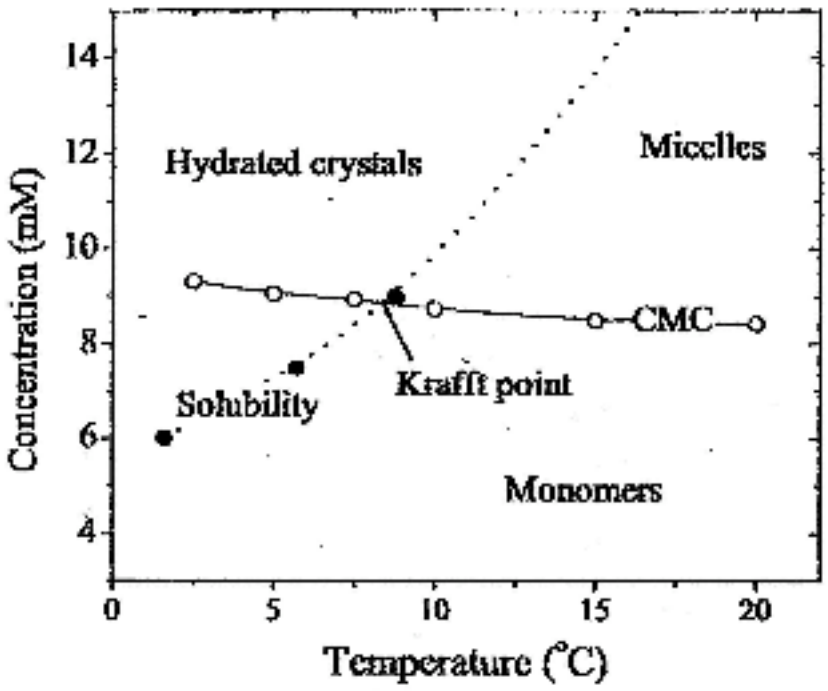


Figure 12.1: Different types of surface active molecules.





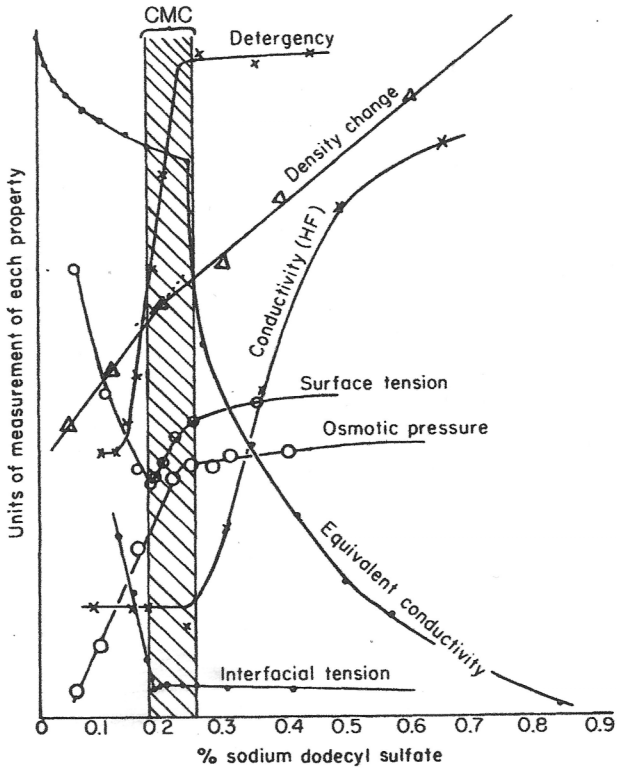
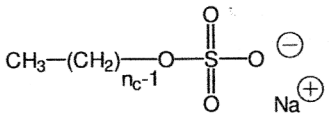
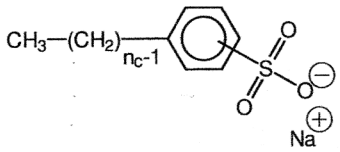
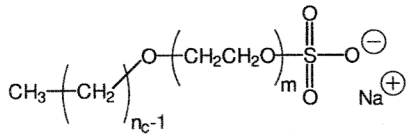
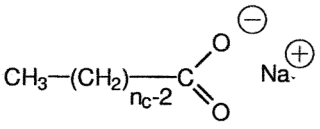
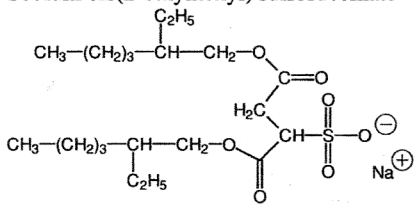
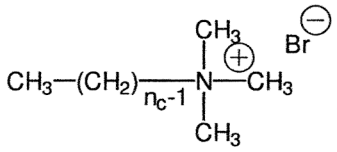
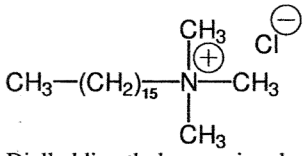
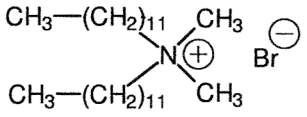
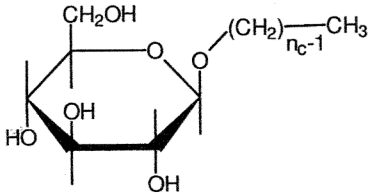
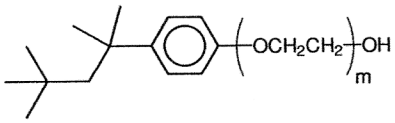
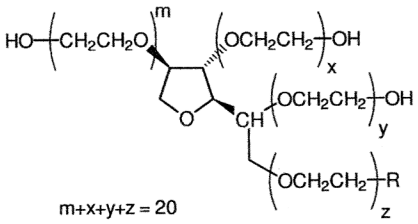
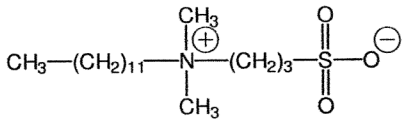


Fig. XIII-10. Properties of colloidal electrolyte solutions—sodium dodecyl sulfate. (From Ref. 102a.)

Table 12.1: Structure of common surfactants and critical micelle concentrations (CMCs in mM) in water at 25°C (no added salt). The CMCs were taken from Refs. [109, 519, 520].

Surfactant		CMC
Anionic		
Sodium alkylsulfate		
	$n_C = 8$, sodium octylsulfate	139
	$n_C = 10$, sodium decylsulfate	34
	$n_C = 11$, sodium undecylsulfate	17
	$n_C = 12$, sodium dodecylsulfate (SDS)	8.9
Sodium alkylbenzenesulfonate		
	$n_C = 7$, sodium heptylbenzene sulfonate	24
	$n_C = 8$, sodium octylbenzene sulfonate	12
	$n_C = 12$, sodium dodecylbenzene sulfonate	3.6
Sodium alkylether sulfate	AES	
	$n_C = 12 - 14$, $m = 2 - 4$	

Surfactant		CMC
Sodium alkylcarboxylate	Sodium salt of	
	$n_C = 10$, decanoic acid	100
	$n_C = 11$, undecanoic acid	50
	$n_C = 12$, dodecanoic (lauric) acid	25
	$n_C = 13$, tridecanoic acid	13
	$n_C = 14$, tetradecanoic (myristic) acid	6.3
	$n_C = 16$, hexadecanoic (palmitic) acid	1.8
	$n_C = 18$, octadecanoic (stearic) acid	
	$n_C = 20$, eicosanoic (arachidic) acid	
	$n_C = 22$, docosanoic (behenic) acid	
Sodium bis(2-ethylhexyl) sulfosuccinate	Aerosol OT (AOT)	1.4
		
Cationic		
Alkyltrimethylammonium bromide	$n_C = 10$, decyl trimethylammonium bromide	66
	$n_C = 12$, dodecyl trimethylammonium bromide	15
	$n_C = 14$, tetradecyl trimethylammonium bromide (TTAB)	3.5
	$n_C = 16$, hexadecyl trimethylammonium bromide (CTAB)	0.9
Alkyltrimethylammonium chloride	hexadecyl trimethylammonium chloride	1.3
		
Dialkyldimethylammonium bromide	didodecyldimethylammonium bromide (DDAB)	0.15
		

Surfactant		CMC
Nonionic		
Alkylethylene glycol		
$C_{10}H_{21}(OCH_2CH_2)_4OH$	$C_{10}E_4$	0.79
$C_{10}H_{21}(OCH_2CH_2)_6OH$	$C_{10}E_6$	0.9
$C_{10}H_{21}(OCH_2CH_2)_8OH$	$C_{10}E_8$	1.0
$C_{12}H_{25}(OCH_2CH_2)_8OH$	$C_{12}E_8$	0.071
$C_{14}H_{29}(OCH_2CH_2)_8OH$	$C_{14}E_8$	0.009
Alkylglucosides 	$n_C = 8$, octyl-β-D-glucoside	25
	$n_C = 10$, decyl-β-D-glucoside	2.2
	$n_C = 12$, dodecyl-β-D-glucoside	0.19
Poly(ethylene oxide) *iso*-octylphenyl ether 	$m = 7, 8$, Triton$^{(R)}$ X-114	0.20
	$m = 10$, Triton$^{(R)}$ X-100	0.24
	$m = 40$, Triton$^{(R)}$ X-405	0.81
Poly(ethylene oxide) sorbitan monoalkanoate 	R=~$OCO(CH_2)_{10}CH_3$: monolaurate Tween$^{(R)}$20	0.08
	R=~$OCO(CH_2)_{16}CH_3$: monostearate Tween$^{(R)}$60	0.0027
Zwitterionic		
Alkyldimethylpropanesultaine 	N-dodecyl-N,N-dimethyl propanesultaine	

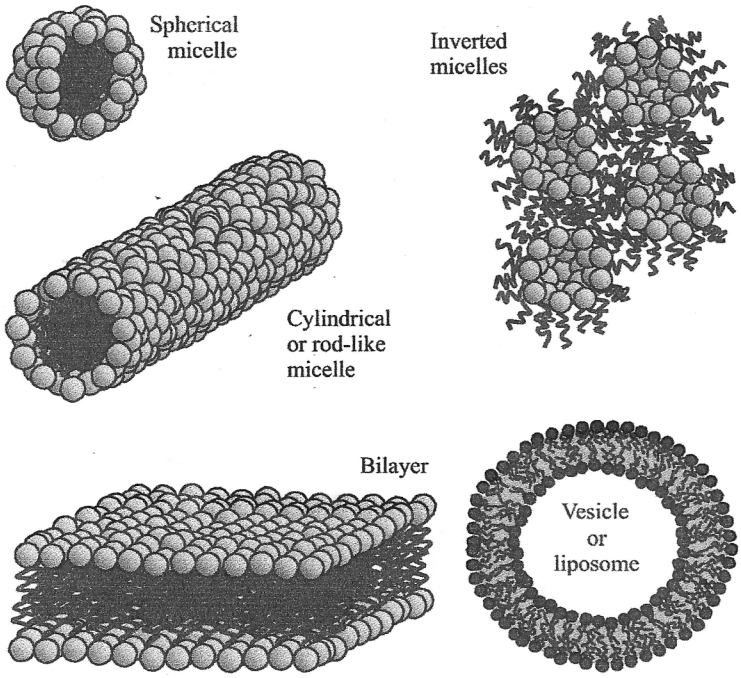


Figure 12.7: Aggregates formed by surfactants.