LECTURE 2
CONTINUED

Pt 2: T.D. OF INTERFACES

- YOUNG-LAPLACE LAW
  REVISITED

  - CONSIDER A SYSTEM OF
    FIXED VOLUME IN THERMAL
    CONTACT W/ A "HEAT
    RESERVOIR", i.e. A SYSTEM
    SO LARGE THAT ITS TEMP-

ERATURE REMAINS CONSTANT
EVEN AFTER LARGE HEAT
TRANSFERS ΔQ.

- THEN WE HAVE: T_R (T FIXED)

$$\Delta\left[u - TS\right] = \Delta u - \cancel{T}\Delta S - S\cancel{\Delta T}$$

$$= -\Delta u_R - T_R\Delta S \qquad \begin{array}{c}\text{ENT. OF}\\\text{SYSTEM.}\end{array}$$
$$\left[\begin{array}{c}1^{ST}\\\text{LAW}\end{array}\right] \qquad \text{ENT. OF RESERVOIR}$$
$$= -T_R\Delta S_R - T_R\Delta S$$

$$= -T_R\left[\underline{\Delta S_R + \Delta S}\right] \leq 0 \quad \left[\begin{array}{c}2^{ND}\\\text{LAW}\end{array}\right]$$
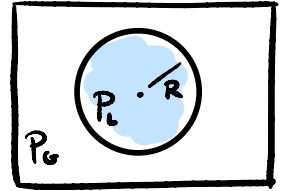$$\qquad\qquad \text{TOTAL ENTROPY}$$

- SO ANY SYSTEM UNDERGOING
A PROCESS @ FIXED VOLUME &
TEMPERATURE WILL EVOLVE TO
MINIMIZE THE "HELMHOLTZ FREE
ENERGY" $F = u - TS$

- CONSIDER A DROP OF LIQUID IN A FIXED VOLUME OF GAS @ FIXED TEMPERATURE:

$$dF_G = d\left[U_G - TS_G\right]$$

$$= \left[dU_G\right] - T\,dS_G$$

$$= \left[T\,dS_G - P_G\,dV_G - \mu_G\,dN_G\right] - T\,dS_G$$

$$= -P_G\,dV_G - \mu_G\,dN_G$$

- LIKEWISE : $dF_L = -P_L\,dV_L$

- AND : $dF_{\underline{S}} = \gamma\,dA$

SURFACE / INTERFACE

- NOW $dV_L = -dV_G$, $dN_L = -dN_G$

& $dV_L = 4\pi R^2\,dR$,

$$dA = 8\pi R\,dR$$

- So: $\partial F = \partial \left[F_G + F_L + F_s \right] = \partial F_G + \partial F_L + \partial F_s$

$$= -\left[P_L - P_G \right] \partial V_L + \gamma \partial A + \left[\mu_L - \mu_G \right] \partial N_L$$

- minimizing F then requires:

   - $\mu_L = \mu_G$

   - $\left[P_L - P_G \right] 4\pi R^2 \partial R = \gamma \, 8\pi R \partial R$

      $$\implies P_L - P_G = 2\gamma / R \quad \checkmark$$

- EULER'S THEOREM
   AND SURFACE ENERGY / ENTROPY

- FOR AN EXTENSIVE FUNCTION
   $Z(x, \ldots, y)$ OF EXTENSIVE
   VARIABLES $x, \ldots, y$ WE HAVE:

$$Z(x, \ldots, y) = Z_x x + \cdots + Z_y y$$

WHERE $dz = Z_x dx + \cdots + Z_y dy$

- SO:

$$U_s = TS_s + \gamma A_s$$

OR $F_s = U_s - TS_s = \gamma A_s$

OR $f_s = \dfrac{F_s}{A_s} = \gamma$

ALSO: $dF_s = \gamma \, dA_s - S_s \, dT$

- EVIDENTLY:

$$\gamma = \dfrac{\partial F_s}{\partial A_s}\bigg|_T \, , \quad S_s = -\dfrac{\partial F_s}{\partial T}\bigg|_{A_s}$$

- NOW, FOR ANY SMOOTH FUNCTION:

$$\frac{\partial}{\partial x}\frac{\partial}{\partial y} z = \frac{\partial}{\partial y}\frac{\partial}{\partial x} z$$

- So that:

$$\left.\frac{\partial \gamma}{\partial T}\right|_{A_s} = -\left.\frac{\partial S_s}{\partial A}\right|_T = -\frac{S_s}{A} = -S_s$$

$$\implies S_s = -\left.\frac{\partial \gamma}{\partial T}\right|_{A_s}$$

- So we can measure surface entropy $\uparrow$ DENSITY by measuring temp dependence of surf-tens!

- Surface energy density can be measured similarly:

$$u_s = \frac{U_s}{A_s} = \frac{F_s + TS_s}{A} = f_s + TS_s$$

$$= \gamma - T\left.\frac{\partial \gamma}{\partial T}\right|_{A_s}$$

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 DIVIDING SURFACE
  & I.F. CHEM. OF SOLUTIONS

- WHERE IS THE INTERFACE, PRECISELY?

- GIBBS DEFINES THE INTERFACE TO BE A SURFACE OF CONSTANT SOLVENT

CONCENTRATION W7 THE
PROPERTY THAT:

$$n_1^G V_1^G + n_1^L V_1^L = N_1$$

- WHERE SUBSCRIPT 1
  DENOTES THE SOLVENT
  SPECIES & n_1^G, n_1^L DENOTING
  RESPECTIVELY THE ASYMPTOTIC NUMBER
  DENSITY OF THE SOLVENT IN
  THE BULK OF THE GAS &
  LIQUID :
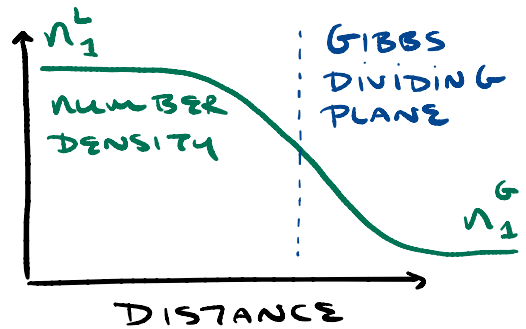
- FOR LIQUID - GAS INTERFACES
  THAT ARE NOT SINGLE - COMP-
  ONENT, WE MUST CONSIDER

SEVERAL CHEMICAL SPECIES
w/ TOTAL MOLE NUMBERS

$$N_1, N_2, \ldots, N_m.$$

SOLVENT SPECIES   SOLUTE SPECIES

- NOW FOR $i \neq 1$ WE HAVE IN GENERAL:

$$\underbrace{n_i^G V_i^G}_{N_i^G} + \underbrace{n_i^L V_i^L}_{N_i^L} \neq N_i$$

- THE DIFFERENCE

$$N_i - \left[N_i^G + N_i^L \right] = N_i^S \quad \text{NORMALIZED}$$

TO THE SURFACE AREA A

IS TERMED THE "SURFACE EXCESS"

$$\Gamma_i = N_i^S / A$$

GIBBS ADSORPTION ISOTHERM

- CONSIDERING NOW A SINGLE SOLUTE SPECIES DISSOLVED IN A SOLVENT, WE NOW NEED TO INCLUDE N_2^s AS A SURFACE STATE VARIABLE ALONG WITH ENTROPY S_s AND AREA A_s

$$dU_s = TdS_s + \gamma dA_s + \mu_2^s dN_2^s \quad (1)$$

- BUT AGAIN FROM EXTENSIVITY:

$$U_s = TS_s + \gamma A_s + \mu_2^s N_2^s$$

$$\Rightarrow dU_s \text{ is ALSO:}$$

$$= TdS_s + S_s dT + \gamma dA_s + A_s d\gamma$$
$$+ \mu_2^s dN_2^s + N_2^s d\mu_2^s \quad (2)$$

- SUBTRACTING (1) FROM (2):

$$d\underline{u}_s - d\underline{u}_s = 0$$

$$\implies S_s dT + A_s d\gamma + N_2^s d\mu_2^s = 0$$

- @ CONST TEMP: $dT \to 0$:

$$d\gamma = -\Gamma_2 \, d\mu_2^s$$

- WHEN INTERFACE IS IN EQUILIBRIUM w/ SOLUTION:

$$\mu_2^s = \mu_2^L = \mu_2^\circ + RT \ln \frac{a}{a_o}$$

  - WHERE a IS THE ACTIVITY OF SOLUTE IN SOLUTION
  $$\left[@ \underset{\wedge \text{SOLUTE}}{\text{LOW}} \text{ CONCENTRATIONS } c, \; a \propto c \right]$$

$$\Rightarrow \quad d\mu_2^S = d\mu_2^L = RT\, d\ln a$$

$$\Rightarrow \quad \begin{array}{l} (3) \\ \text{"GIBBS} \\ \text{ISOTHERM"} \end{array} \left[\begin{array}{l} \Gamma_2 = -\dfrac{1}{RT} \dfrac{\partial \gamma}{\partial \ln a}\bigg|_T \\[2ex] \text{OR} \quad = -\dfrac{a}{RT} \dfrac{\partial \gamma}{\partial a}\bigg|_T \end{array} \right]$$

- MICELLES

- THE FOLLOWING PLOT SHOWS
  THE MEASURED SURFACE
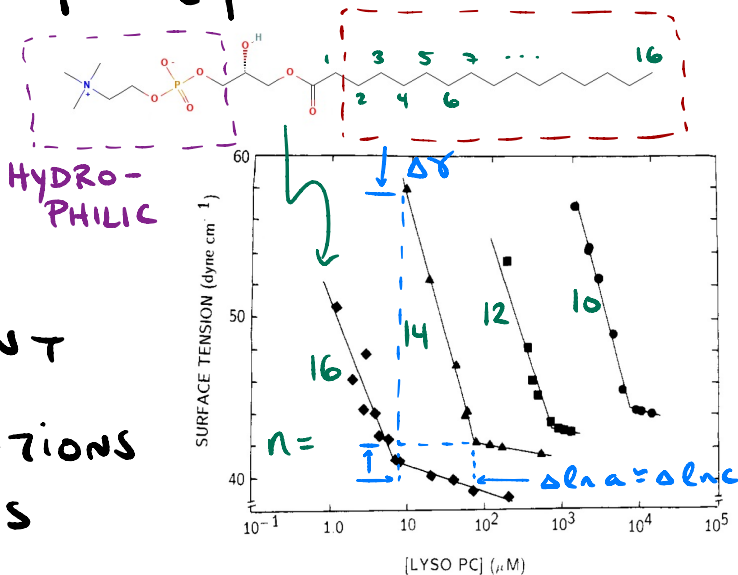 TENSION OF DIFFERENT
  "LYSOPHOSPHOLIPIDS"
  W/ FATTY
  ACID CHAIN
  LENGTH n

  @ DIFFERENT

  CONCENTRATIONS

  IN AQUEOUS

  SOLUTION:

HYDROPHOBIC

HYDRO-
PHILIC

$n=$

$\Delta\gamma$

16

14

12

10

$\partial \ln a = \partial \ln c$

SURFACE TENSION (dyne cm^{-1})

[LYSO PC] (μM)

- SINCE THE MOLECULES HAVE A SURFACTANT-LIKE HYDROPHILIC + HYDROPHOBIC STRUCTURE, IT IS NOT SURPRISING THAT WE OBSERVE A DECREASE IN SURF. TENS. w/ INC. PHOSPHO-LIPID CONCENTRATION.

- SETTING ASIDE FOR THE MOMENT THE DISCONTINUITY IN THE SLOPE @ HIGHER CONCS, WE CAN EVIDENTLY APPLY THE GIBB'S ISOTHERM TO ESTIMATE THE SURFACE EXCESS:

- TAKING THE $n = 14$ ["TETRA-DECA"] PHOSPHOLIPID DATA:

- $\Gamma_2 = -\dfrac{1}{2.5\ kJ/mol} \times \dfrac{(58-42)\ mN/m}{\left[\ln 10^1 \mu M - \ln 10^{1.8} \mu M\right]}$

$\qquad = +\dfrac{1\ mol}{2.5\times 10^3\ J} \times \dfrac{16\times 10^{-3}\ J/m^2}{+0.8 \times \ln 10}$

$\qquad = 3.6 \times 10^{-6}\ mol/m^2$

$\qquad = \dfrac{3.6 \times 10^{-6} \times 6\times 10^{23}\ MOLECULES}{10^{20}\ \mathring{A}^2}$

$\qquad = 0.021\ MOLECULES/\mathring{A}^2$

OR: $\qquad 50\ \mathring{A}^2/MOLECULE$

- AND WHAT ABOUT THE "KINK" IN THE SLOPE @ HIGHER CONCEN-TRATIONS?

- "MICELLE" FORMATION IN SOLUTION:

-

SURFACE EXCESS

AIR-WATER INTERFACE

INCREASING CONCENTRATION

MICELLES

MONOMERS
(I.E. SINGLE PHOSPHOLIPIDS)

E.G. $\nu = 10$ PHOSPHOLIPIDS
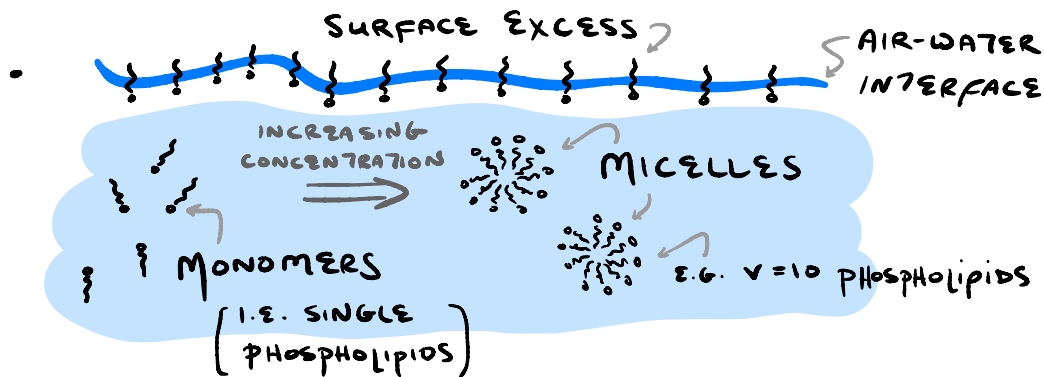
- MASS ACTION:

  - CHEMICAL REACTION IN SOLUTION:

    - $\nu m \longleftrightarrow M$
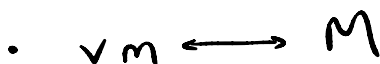
  $\longrightarrow$: "ν MONOMERS CLUSTER TO FORM ONE MICELLE"

  $\longleftarrow$: "ONE MICELLE DISSOCIATES INTO ν MONOMERS"

  - IF c & c' ARE RESP. THE CONCENTRATIONS OF (IN MOLS/LITER) MONOMERS AND MICELLES, THEN FROM LAW OF MASS ACTION WE HAVE:

$$\frac{c^\nu}{c'} = \exp\left[\Delta G^\circ \big/ RT\right]$$

$$= K \longleftarrow \text{EQUILIBRIUM CONST.}$$

ΔG°
$=$
$G^\circ_{MICELLE} - \nu G^\circ_{MONOMER}$
@ $c' = 1$ @ $c = 1$
"STANDARD GIBBS"

- @ SUFFICIENTLY LOW MONOMER CONC., WE WILL CLEARLY HAVE NO MICELLES:

$$\lim_{c \to 0} \frac{c'}{c} \propto \lim_{c \to 0} \frac{c^\nu}{c} = \lim_{c \to 0} c^{\nu-1} = 0 \quad \text{FOR } \nu > 1$$

- **@ WHAT CONC. DO WE START TO HAVE SIGNIFICANT MICELLE CONTENT ?**

  - ASKED ANOTHER WAY:

    - SUPPOSE WE ADD A SMALL AMOUNT ε OF MONOMERS TO SOLUTION.

      - A FRACTION X OF THESE MOLECULES WILL GO TOWARDS FORMATION OF NEW MICELLES, WHILE THE REMAINING FRACTION $1-x$ STAY AS MONOMERS.

$$\varepsilon \quad \begin{cases} \to \varepsilon(1-x) \text{ MONOS} \\ \to \varepsilon x/v \text{ MICELLES} \end{cases}$$

      - X DEPENDS ON THE EXISTING CONC.

        - E.G. WE SAID $X \to 0$ AS $C \to 0$.

      - @ WHAT CONC. DOES $X = 50\% ?$

  - $\dfrac{c^{\vee}}{c'} = K = \dfrac{[c + \varepsilon(1-x)]^{\vee}}{c' + \varepsilon x/v}$

  $\left[\begin{array}{c} \text{FOR} \\ \text{SMALL} \\ \varepsilon \end{array}\right] \approx \dfrac{c^{\vee}}{c'} \times \dfrac{1 + \frac{v\varepsilon}{c}(1-x)}{1 + \varepsilon x/vc'}$

$$\implies \frac{v}{c}(1-x) = \frac{x}{vc'}$$

$$\implies x = \left[1 + \frac{1}{v^2} \times \frac{c}{c'} \right]^{-1} \quad (3)$$

SO IF $x = \frac{1}{2} \implies c' = \frac{c}{v^2}$

- SO WHEN #MONOMERS IN MICELLES
$$= \frac{1}{v} \times \text{\# MONOMERS } \cancel{\emptyset} \text{ IN MICELLES.}$$

- @ $x = \frac{1}{2}$ WE THUS HAVE:

$$\frac{c^v}{c/v^2} = EXP\left(\frac{\Delta G^\circ}{RT} \right)$$

$$\implies RT \ln c = -\frac{2 \ln v}{v-1} RT + \frac{\Delta G^\circ}{v-1} \left. \begin{cases} \text{≗ STD. GIBBS} \\ \text{RXN ENERGY} \\ \text{PER MOLE F} \\ \text{MONOMER} \end{cases} \right.$$

- FOR $\Delta G^\circ \gg RT$ WE NEGLECT THE $\ln v$ TERM.

$\curvearrowleft$ ["CMC"]

- SO @ THE "CRITICAL MICELLE CONCENTRATION"

(5) $C_{CMC} \approx EXP\left(\Delta G^\circ / vRT \right)$ THE MONOMERS

BECOME UNSTABLE W/ RESPECT TO THE

FORMATION OF SMALL GLOBULAR HYDRO-PHOBIC/

HYDROPHILIC INTERFACES, I.E. MICELLES.

- @ "TOTAL MONOMER CONC." $c + vc' \gg C_{cmc}$, WE EXPECT $x \to 100\%$, SO THAT ADDING MORE SURFACTANT WILL HAVE NO EFFECT ON THE MONOMER CONC. c IN SOLUTION.

- THIS EXPLAINS THE "FLATTENING" OF THE γ VS. CONCENTRATION CURVES SHOWN ABOVE:
  - ↑ONLY Γ IS SENSITIVE TO MONOMER CONC c, NOT TOTAL CONC. $c + vc'$.

- THERE IS STILL THE LINGERING QUESTION OF WHY THE MONOMER $\to$ MICELLE TRANSITION @ $c \simeq C_{cmc}$ IS APPARENTLY DISCONTINUOUS.

- LET'S LOOK @ HOW x CHANGES FOR A SMALL FRACTIONAL CHANGE IN CONC NEAR : $c = C_{cmc}$

$\bullet \quad c \to (1+\alpha)\, c_{cmc}, \quad \alpha \ll 1$

$$\Rightarrow c' \to \underline{c_{cmc}}_{v^2} + \alpha \underline{c_{cmc}}_{v} = \underline{c_{cmc}}_{v^2}\left[1 + v\alpha\right]$$

WHY? $\bullet \quad @ \quad \alpha \to 0 \quad c = c_{cmc}$

$$\Rightarrow x = \tfrac{1}{2}$$

$$\Rightarrow c' = \frac{c}{v^2} = \frac{c_{cmc}}{v^2}$$

$\bullet$ SINCE $x \simeq \tfrac{1}{2}$, AN INCREASE Δc

IN c implies AN INCREASE $\Delta c' = \dfrac{\Delta c}{v}$

IN c'.

FROM (4):

$\bullet \quad x = \tfrac{1}{2} + \Delta x = \left[1 + \dfrac{(1+\alpha)\,c_{cmc}}{v^2\,\dfrac{c_{cmc}}{v^2}(1+v\alpha)}\right]^{-1}$

FOR $\alpha \ll 1:$

$$\simeq \left[1 + (1+\alpha)(1 - v\alpha)\right]^{-1}$$

$$\simeq \left(2\left[1 - \left(\tfrac{v-1}{2}\right)\alpha\right]\right)^{-1}$$

$$\simeq \tfrac{1}{2}\left[1 + \left(\tfrac{v-1}{2}\right)\alpha\right]$$

$$\Rightarrow \left.\frac{dx}{d\alpha}\right|_{c=c_{cmc}} = \tfrac{1}{4}(v-1)$$
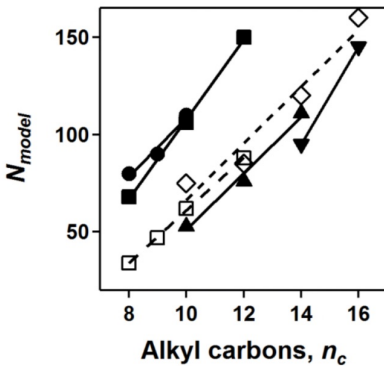
1.2. v

$\bullet$ SO: THE **BIGGER** THE MICELLE, THE

THE **FASTER** THE TRANSITION $x = 0\% \to 100\%$!

- A MORE COMPLETE NUMERICAL SOLUTION OF THE MODEL GIVES:

x versus concentration

distribution fraction x vs total monomer concentration $c + \nu c'$, units of c_{CMC}

micelle size ν: 2, 8, 32, 128
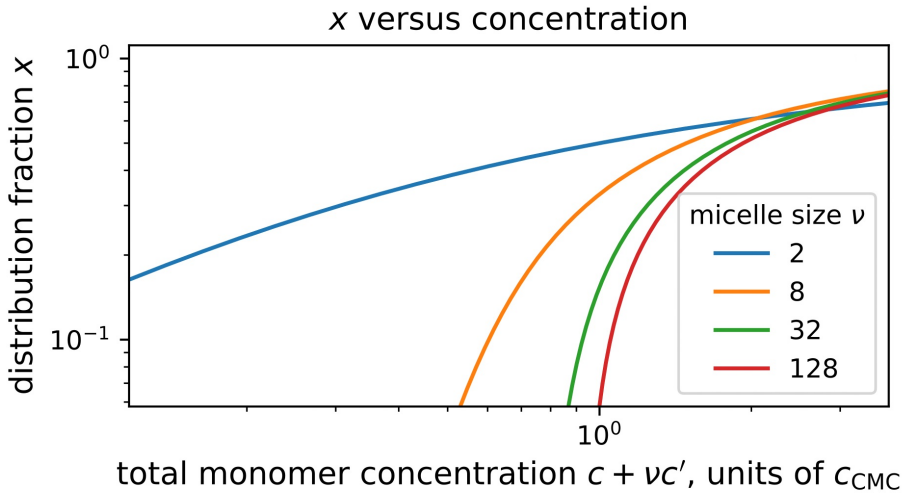
- TYPICAL MICELLE SIZES ARE QUITE LARGE: $\nu \simeq 50 - 150$:

HERE IS A PLOT OF "MONOMER NUMBER" [WHAT WE CALL ν] AS ESTIMATED FROM X-RAY SCATTERING FOR DIFF. DETERGENT MONOMERS VS. HYDROPHOBIC TAIL LENGTH n_c SEE CITED ARTICLE FOR DETAILS.

* IS THE $N_c = \nu \propto n_c$ CORRELATION IN LINE W/ YOUR EXPECTATIONS?