Surface Tension Measurement and Adsorption Isotherm Determination Using the Drop Weight Method

Teng-Jui Lin
Department of Chemical Engineering, University of Washington

Surface and Colloid Science

Surface tension calculation from the drop weight method

- Tate (1864)

$$W = 2\pi r\sigma$$

$W = F_{net} = |\rho_2 - \rho_1| V g$

$F_{buoy} = \rho_2 V g$

$F_g = mg = \rho_1 V g$

$\sigma 2\pi r$

$F_g = W$

- Harkins and Brown (1919)

$$W = 2\pi r\sigma f = \frac{r\sigma}{F} \Rightarrow \sigma = \frac{WF}{r} = \frac{|\rho_2-\rho_1|Vg}{r}$$

$$F \equiv \tfrac{1}{2}\pi f = \text{function of } (r, V$$

- Heertjes et al. (1971)

$$F = 0.14782 + 0.27896\left(\frac{r}{V^{1/3}}\right) - 0.1662\left(\frac{r}{V^{1/3}}\right)^2$$

Constraint: $\left(\frac{r}{V^{1/3}}\right) \in (0.3, 1.2)$

- Surface tension

$\rho_2 \equiv \rho$ $\quad m = \rho V$

$$\sigma = \frac{V|\rho_2 - \cancel{\rho_1}^{\,0}|gF}{r} = \frac{V\rho g F}{r} = \frac{mgF}{r}$$

$$\boxed{\sigma = \frac{mgF}{r}}$$

$* F(r, V^{1/3})$

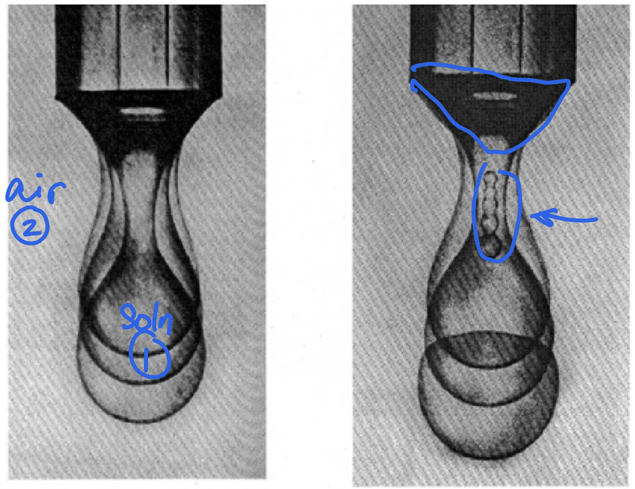
need ρ

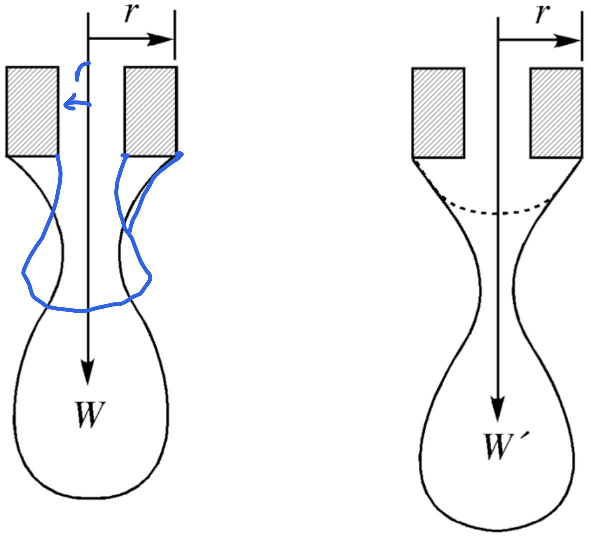
measure: replaced by m

droplet's ρ, V, r

know: g

soln





Szyszkowski equation describes surface tension of binary aqueous solutions

- Szyszkowski equation : $\sigma(m_2)$

molality (mol/kg) of the solute

$$\sigma = \sigma_0 - RTB \ln\left(1 + \frac{m_2}{a}\right)$$

surface tension

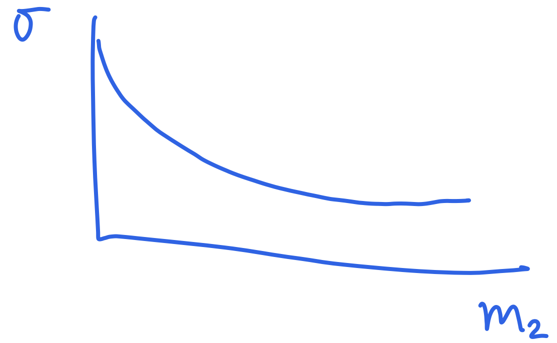
" of pure solvent

ideal gas const

absolute temp.

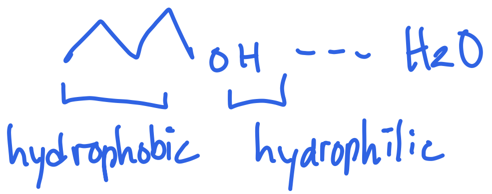
$R = 8.314$ J/mol K

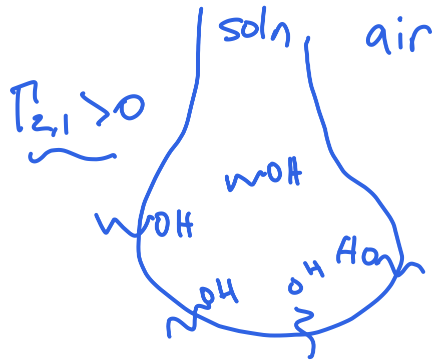
a, B, empirical const.



Adsorption isotherm is modeled by Gibbs adsorption equation

alcohol aq soln





isothermal

- Gibbs adsorption equation: ideal solution

relative adsorption

$$\underbrace{\Gamma_{2,1}}_{\text{solute, solvent}} = -\frac{x_2}{RT}\frac{d\sigma}{dx_2}$$

$d\sigma$ — surface tension

dx_2 — mol frac of solute

- Gibbs adsorption equation: ideal dilute solution

$$\Gamma_{2,1} = -\frac{m_2}{RT}\frac{d\sigma}{dm_2}$$

dm_2 — molality (mol/kg)

- General Gibbs adsorption equation

$$\Gamma_{2,1} = -\frac{m_2}{RT\left[1 + \dfrac{d\ln\gamma_2^H}{d\ln m_2}\right]}\frac{d\sigma}{dm_2}$$

γ_2^H — activity coeff based on Henry's law

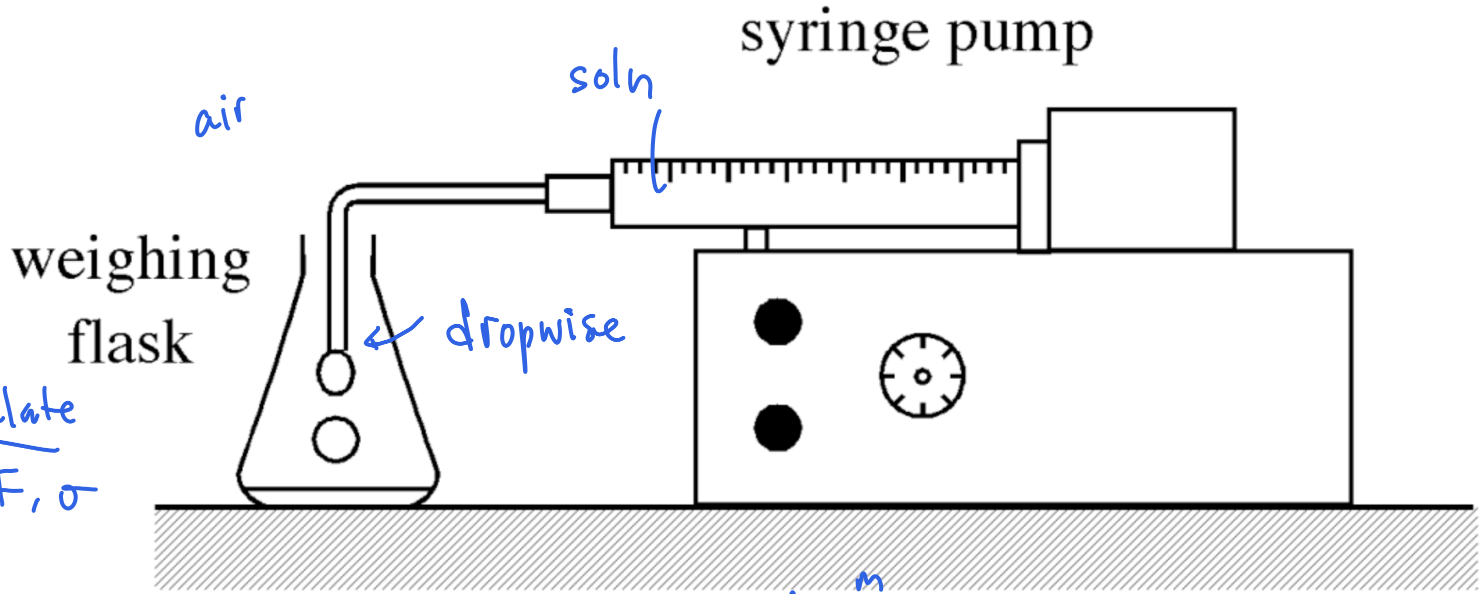
if $\gamma_2^H \neq f(m_2)$

$$\frac{d\ln\gamma_2^H}{d\ln m_2} \rightarrow 0$$

$\Gamma_{2,1} > 0 \Rightarrow$ interfacial layer is enriched of comp 2 than the bulk phase

$\Gamma_{2,1}(m_2)$

Objective: Determining concentration dependence of surface tension



~10 drops

measure: m, ρ

calculate: V, F, σ

known: r, g

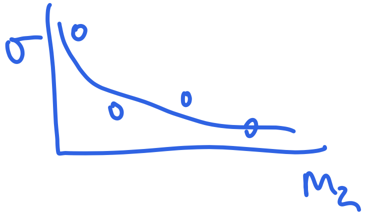
$\rho = \frac{m}{V}$

$V = \frac{m}{\rho}$

- Surface tension of water and aqueous solutions
  - $\sigma = \dfrac{mg}{r} F(r, V)$
  - $F = 0.14782 + 0.27896 \left(\dfrac{r}{V^{1/3}}\right) - 0.1662 \left(\dfrac{r}{V^{1/3}}\right)^2$

measure σ, σ_ρ

- Surface tension of aqueous n-butanol solution vs. concentration
  - Determine Szyszkowski parameters a and B
  - $\sigma = \sigma_0 - RTB \ln\left(1 + \dfrac{m_2}{a}\right)$



known: R, m_2

measure: T, σ_0

calculate: $\sigma(m_2)$

Objective: Constructing adsorption isotherms

$\Gamma_{2,1}$

- Relative adsorption of n-butanol at air-water interface vs. concentration (adsorption isotherm)

m_2

- Ideal dilute Gibbs adsorption equation

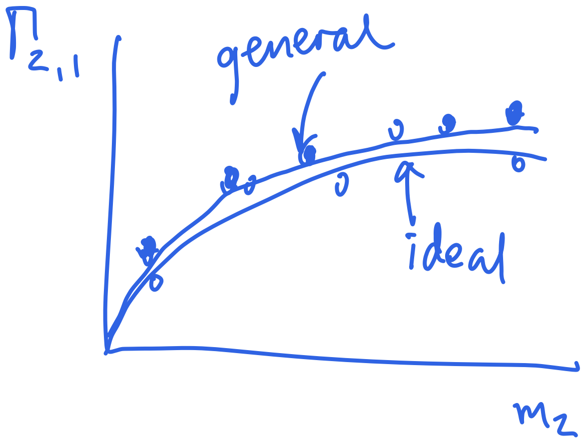
$$\checkmark\ \Gamma_{2,1} = -\frac{m_2}{RT}\frac{d\sigma}{dm_2}$$

- General Gibbs adsorption equation

$$\checkmark\ \Gamma_{2,1} = -\frac{m_2}{RT\left[1+\boxed{\dfrac{d\ln\gamma_2^H}{d\ln m_2}}\right]}\frac{d\sigma}{dm_2}$$

isothermal condition

$\Delta T = 0$



Molality m_2	$\ln(m_2)$	Activity Coefficient γ_2^H	$\ln(\gamma_2^H)$
0.003		0.9971	
0.006	A	0.9942	B
0.010		0.9906	
0.020	C	0.9823	D
0.030		0.9753	
0.040		0.9691	
0.050		0.9638	
0.070		0.9546	
0.100		0.9433	
0.150		0.9276	
0.200		0.9161	
0.250		0.9058	

$\dfrac{D-B}{C-A}$ at $m_2 = 0.01$

Measure	Known	Calculating
T	m_2, R	$\Gamma_{2,1}$

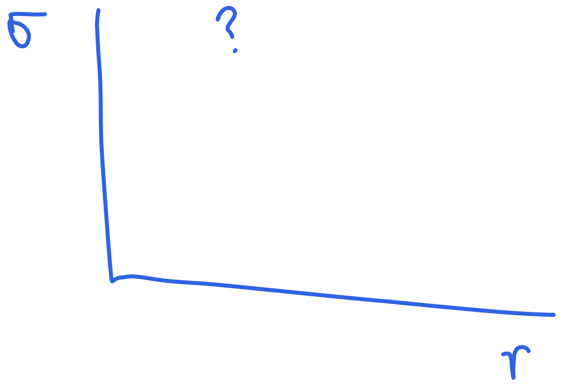
$\dfrac{d\sigma}{dm_2} =$

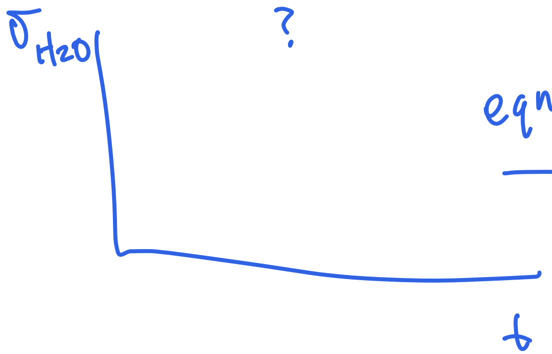
m_2	σ
1	1
2	2
3	3

$\dfrac{\sigma_2 - \sigma_1}{m_{2,2} - m_{2,1}}$

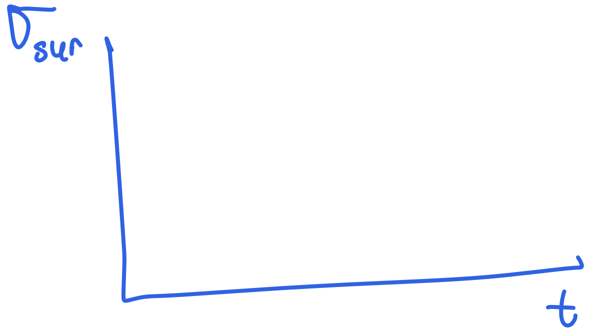
Objective: Determining factors affecting surface tension

- Surface tension of water vs. nozzle size
- Surface tension of water vs. drop formation time
- Surface tension of 0.01 mM Triton X-100 surfactant solution vs. drop formation time
- Compare surface tension measured by various techniques
    - Drop weight, du Noüy ring, Wilhelmy slide, sessile/pendant drop





eqm better →



- "actual" surface tension - "truth" thermo property - doesn't dep on measurement method
- apparent surface tension - what we measured - DOES dep on measurement method

r, t