Interfacial Tension Measurement and Adsorption Isotherm Determination Using the Inverted 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)

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

- Harkins and Brown (1919)

$$W = 2\pi r\sigma \underset{=}{f} = \frac{r\sigma}{F}$$

$$F \equiv \tfrac{1}{2}\pi f$$

$f = \dfrac{\text{W of liq breaks away}}{\text{W of pendant drop}}$

$\sigma = \dfrac{WF}{r} = \dfrac{|\rho_1-\rho_2| g V \cdot F}{r}$

$= \rho_1 g V$

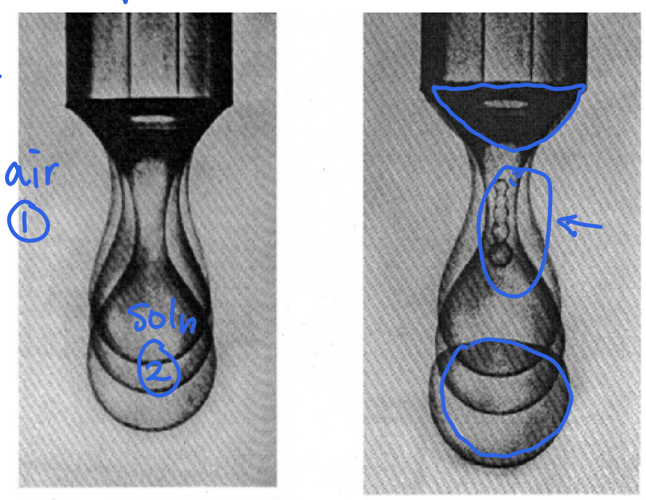
F_{buoy}

$W = mg$

$= \rho_2 V g$

$\sigma P = \sigma 2\pi r$

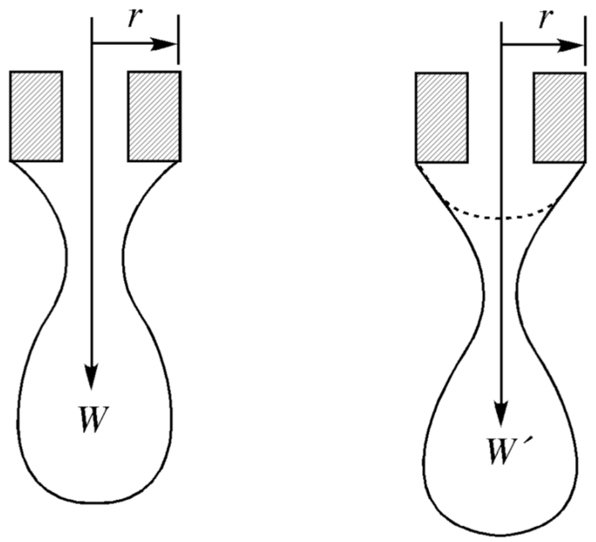
$F_g = W$



- Heertjes et al. (1971)

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

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



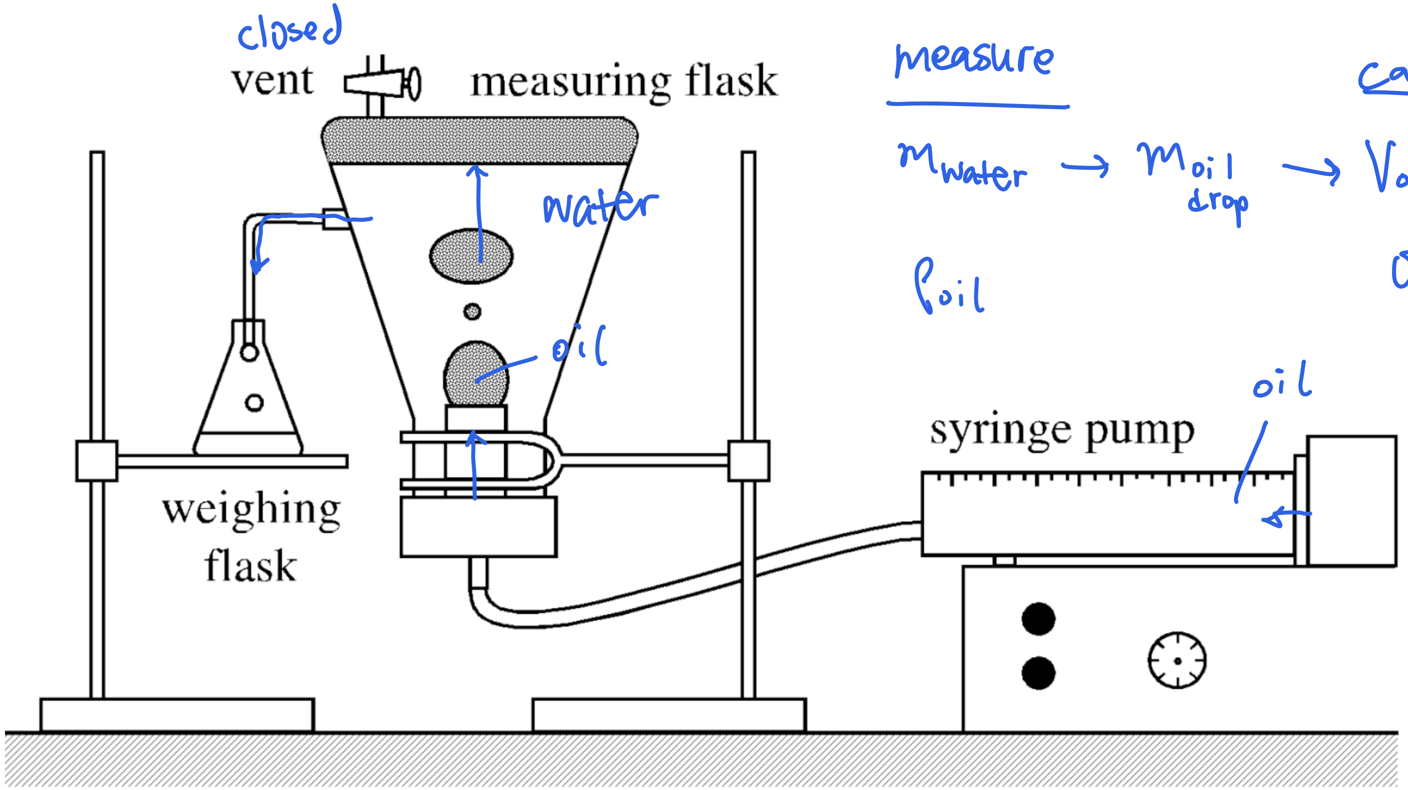
- Surface tension

$$\boxed{\sigma = \frac{V|\rho_2 - \rho_1|gF}{r}}$$

if $\rho_1 \to 0$, $\rho_2 \equiv \rho$

$= \dfrac{V\rho g F}{r} = \dfrac{mgF}{r}$

Interfacial tension between liquids is measured with inverted drop weight method



measure | calculated | know

$m_{water} \rightarrow m_{oil\ drop} \rightarrow V_{oil}, F$ | r, g

ρ_{oil} | σ | ρ_{water}

- Interfacial tension $F = f(r, V)$
  - $\sigma = \dfrac{V|\rho_2 - \rho_1| g F}{r}$
  - $F = 0.14782 + 0.27896\left(\dfrac{r}{V^{1/3}}\right) - 0.1662\left(\dfrac{r}{V^{1/3}}\right)^2$

Szyszkowski equation describes surface tension of binary aqueous solutions

- Szyszkowski equation

a, B empirical const

$$\sigma = \sigma_0 - RTB \ln\left(1 + \frac{C_2}{a}\right)$$

surface tension

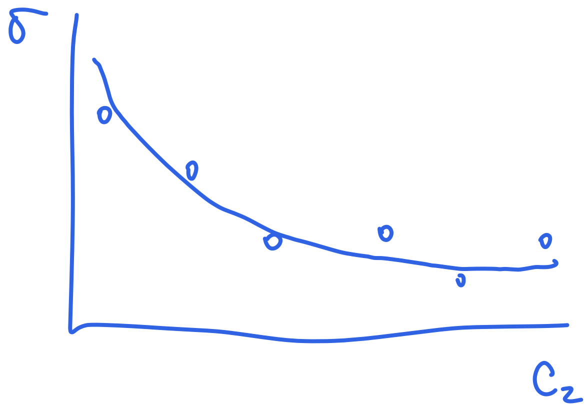
" of pure solvent

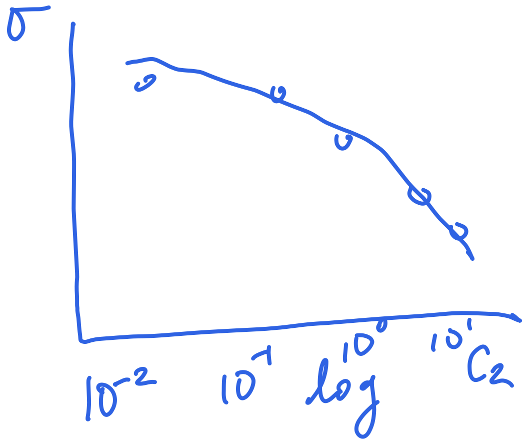
ideal gas const

abs temp

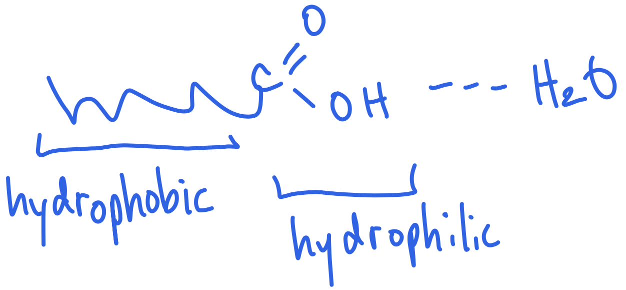
Concentration (molarity) of solute

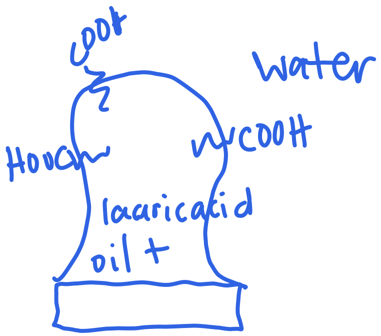
$R = 8.314$ J/mol K





Lauric acid





Adsorption isotherm is modeled by Gibbs adsorption equation

- Gibbs adsorption equation: ideal dilute solution

relative adsorption of solute with respect to solvent

$$\Gamma_{2,1} = -\frac{C_2}{RT}\left(\frac{d\sigma}{dC_2}\right)$$

- Finite difference method

$$\frac{d\sigma}{dC_2} = \frac{\Delta\sigma}{\Delta C_2} = \frac{\sigma_2 - \sigma_1}{C_{2,2} - C_{2,1}}$$

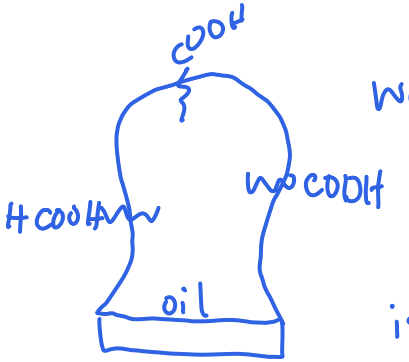
- Szyszkowski equation

$$\sigma = \sigma_0 - RTB\ln\left(1 + \frac{C_2}{a}\right)$$

data - noisy

C_2	σ
1	1
2	2
3	3
4	4

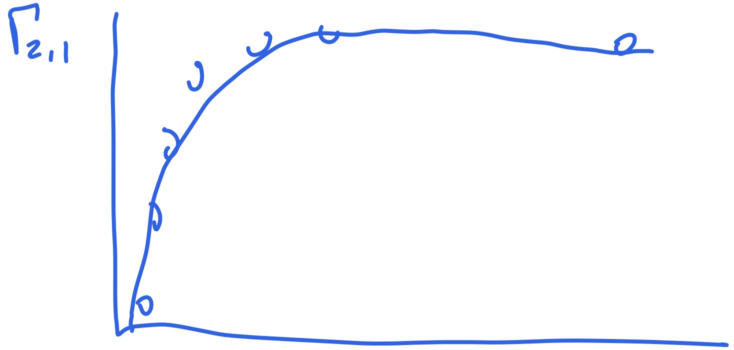
$$\frac{d\sigma}{dC_2} \qquad \frac{3-1}{3-1} = 1$$



water

isothermal cond

$\Delta T = 0$



$$\frac{d\sigma}{dC_2} = \frac{d}{dC_2}\left(\sigma_0 - RTB\ln\left(1 + \frac{C_2}{a}\right)\right)$$

$$= -RTB\,\frac{1/a}{1+\frac{C_2}{a}}$$

$$\hookrightarrow \Gamma_{2,1} = -\frac{C_2}{RT}\frac{d\sigma}{dC_2} = +\frac{C_2}{\cancel{RT}}\left(+\cancel{RT}B\,\frac{1}{a}\,\frac{1}{1+\frac{C_2}{a}}\right) = \frac{C_2B}{a\left(1+\frac{C_2}{a}\right)} = \frac{C_2B}{a+C_2}$$

continuous