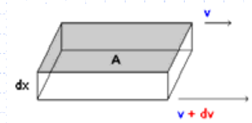
# Physical Chemistry

Lecture 3
Viscosity and sedimentation

## Viscosity

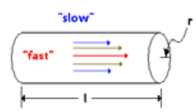
- Fluids resist a gradient of flow
  - Tries to achieve constant speed across the sample
- This resistance creates a force called the viscous drag
- η ≡ viscosity coefficient (or just viscosity)
- Viscosity is measured in poise ($10^{-1}$ kg $m^{-1}$ $s^{-1}$)




$$F_{drag} = \eta A \frac{dv}{dx}$$

## Measurement of viscosity

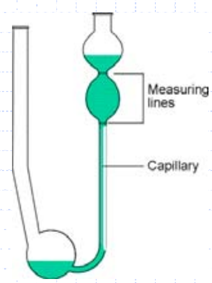
- Measure flow in the presence of a gradient of speed
- Poiseuille's formula for flow through a cylindrical tube subject to a pressure drop




$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{8\eta l}\Delta P$$

## Ostwald viscometer

- Need a small-diameter tube (capillary)
- Measure time of flow of a specific volume through the capillary
- Constant pressure drop across the capillary
- Use Poiseuille's equation to calculate viscosity
- Must be calibrated with a known material

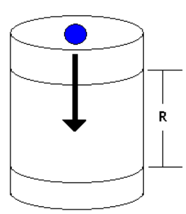



$$t = B\frac{\eta}{\rho}$$

## Falling-ball viscometer

- Measure the terminal velocity of a ball falling in a fluid
- Use Stokes Law for the viscous drag to determine viscosity

$$v_t = \frac{R}{t}$$




$$\eta = \frac{2}{9} r^2 (\rho - \rho_0) \frac{g}{R} t$$

## Origins of viscosity

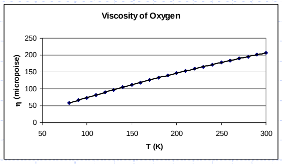
- Liquids
  - Short-range attractive intermolecular forces
    - Hard to model exactly
    - Described empirically
  - Viscosity usually decreases with increasing T
- Gases
  - Momentum transfer between "fast" and "slow" molecules
  - Simple kinetic theory gives a prediction

$$\eta = \frac{n^* < v > m\lambda}{2} = \sqrt{\frac{mkT}{\pi^3 d^4 N_0}}$$

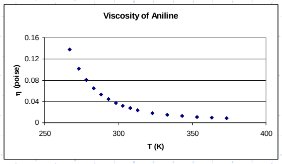
  - Predicts an increase with temperature

## Comparison of temperature-dependent viscosities

- Gas: oxygen
  - Increase with temperature

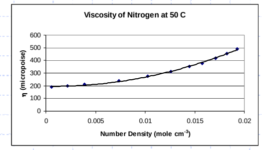



- Liquid: aniline
  - Decrease with temperature




## Intermolecular forces – Enskøg's relation

- Simple kinetic theory predicts no particular density dependence of gas viscosity
- Inclusion of excluded-volume interactions by Enskøg gives a density dependence for the viscosity of a gas



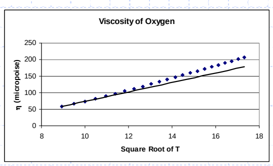

$$\eta = \eta_0\left[1 + 0.175\left(\frac{b_0}{V_m}\right) + 0.865\left(\frac{b_0}{V_m}\right)^2\right]$$

## Including attractive forces – Sutherland's equation

- Approximate potential by Sutherland incorporates attractive forces

$$\eta = \left(\frac{\sqrt{RM}}{\pi^{3/2} d}\right)\frac{\sqrt{T}}{1+\frac{S}{T}}$$

- Example: oxygen viscosity as a function of square root of the temperature




## Viscosity of polymer solutions

- Viscosity of a solution depends on
  - Nature of materials in solution
  - Amount of each material in solution
- Example: polymers in solution with a small-molecule solvent
  - Einstein's relation for a solution of solid balls

$$\eta = \eta_0\left[1 + 2.5\phi_V\right]$$

  - $\phi_V$ is the volume fraction

## Viscosity of polymer solutions

- Specific viscosity, $\eta_{sp}$

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \approx \frac{10\pi r^3}{3m} c_m$$

- Intrinsic viscosity, $[\eta]$

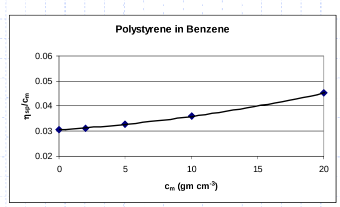
$$[\eta] = \lim_{c_m \to 0} \frac{\eta_{sp}}{c_m}$$

- Mark-Houwink equation

$$[\eta] = K M^{\alpha}$$

## Viscosity of polymer solutions

- Example: polystyrene in benzene (from Noggle)
- Intercept gives intrinsic viscosity
- One may calculate the viscosity-average molecular weight from $[\eta]$ with the Mark-Houwink equation

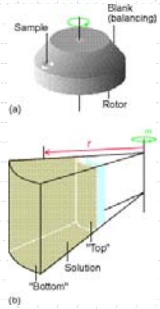


## Sedimentation

- Particles settle in a force field based on mass
- Measure the settling speed to determine mass
- Use centrifugal motion as the force

$$\ln\left(\frac{r}{r_0}\right) = \omega^2 St$$

- unit: Svedberg = $10^{-13}$ sec



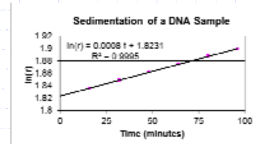

## Sedimentation Coefficient

- Data from Tinoco, Sauer, and Wang, for a DNA sample
- Plot according to equation

$$\ln\left(\frac{r}{r_0}\right) = \omega^2 St$$

- Slope gives S, if the frequency is known
- Frequency in rad/sec

| Time (min) | r (cm) | ln r |
|---|---|---|
| 16 | 6.2687 | 1.836 |
| 32 | 6.3507 | 1.849 |
| 48 | 6.438 | 1.862 |
| 64 | 6.5174 | 1.874 |
| 80 | 6.6047 | 1.888 |
| 96 | 6.6814 | 1.899 |




## Sedimentation Coefficient

- Used for determining molar mass
- Example from Reisner, Rowe, and Macindoe, *J. Mol. Biol.*, *32*, 587 (1968).
  - Ribosomes
    - T = 20°C
    - S = 82.6 Sv
    - D = $1.52\times10^{-7}$ $cm^2\,s^{-1}$
    - V = 0.61 $cm^3\,g^{-1}$

$$M = \frac{SRT}{D(1-\bar{V}\rho)} = \frac{82.6\times10^{-13}s(8.3144349\,J\,K^{-1}mol^{-1})(293K)}{(1.52\times10^{-11}m^2s^{-1})(1-(0.61cm^3g^{-1}0.99808\,g\,cm^{-3}))} =$$
$$= 3.394\times10^3 kg\,mol^{-1}$$

## Summary

- Movement of molecules under forces
  - Viscous flow
  - Sedimentation
- Useful in characterizing the material
  - Viscosity coefficient is a material property
  - Sedimentation coefficient, S, depends on molar mass