

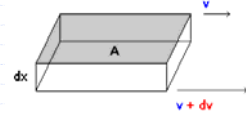
Physical Chemistry

Lecture 3

Viscosity and sedimentation

Viscosity

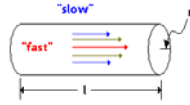
- Fluids resist a gradient of flow
 - ▀ Tries to achieve constant speed across the sample
- This resistance creates a force called the **viscous drag**
- η = viscosity coefficient (or just viscosity)
- Viscosity is measured in **poise** ($10^{-1} \text{ kg m}^{-1} \text{ s}^{-1}$)



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

Measurement of viscosity

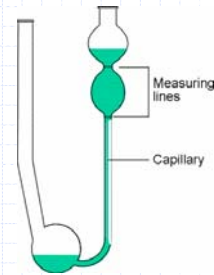
- Measure flow in the presence of a gradient of speed
- Poiseuille's formula for flow through a cylindrical tube subject to a pressure drop



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

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

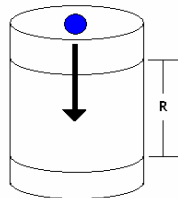


$$t = B \frac{\eta}{\rho}$$

Falling-ball viscometer

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

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



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

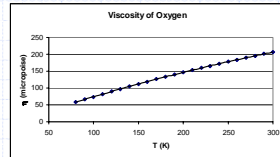
Origins of viscosity

- 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

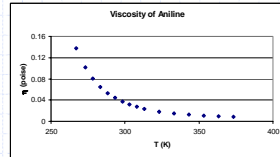
$$\eta = \frac{n \bar{v} m \lambda}{2} = \sqrt{\frac{mkT}{\pi^3 \sigma^4 L}}$$
 - Predicts an increase with temperature

Comparison of temperature-dependent viscosities

- ◆ Gas: oxygen
 - Increase with temperature

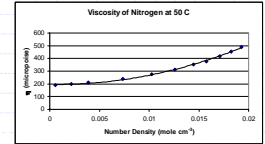


- ◆ Liquid: aniline
 - Decrease with temperature



Intermolecular forces – Enskog's relation

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

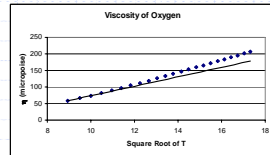


$$\eta = \eta_0 \left[1 + 0.175 \left(\frac{b_0}{V_m} \right) + 0.865 \left(\frac{b_0}{V_m} \right)^2 \right]$$

Including attractive forces – Sutherland's equation

- ◆ Approximate potential by Sutherland incorporates attractive forces
- ◆ Example: oxygen viscosity as a function of square root of the temperature

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



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

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

- ϕ_V is the volume fraction

Viscosity of polymer solutions

- ◆ Specific viscosity, η_{sp}

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

- ◆ Intrinsic viscosity, $[\eta]$

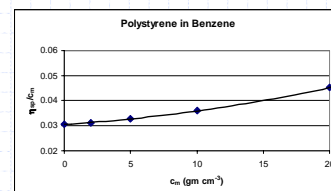
$$[\eta] = \lim_{c_m \rightarrow 0} \frac{\eta_{sp}}{c_m}$$

- ◆ 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

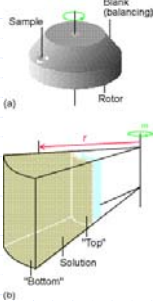


Sedimentation

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

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

- ◆ unit: Svedberg = 10^{-13} sec



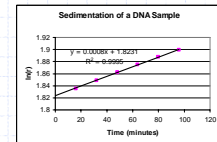
Sedimentation Coefficient

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

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

- ◆ 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



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