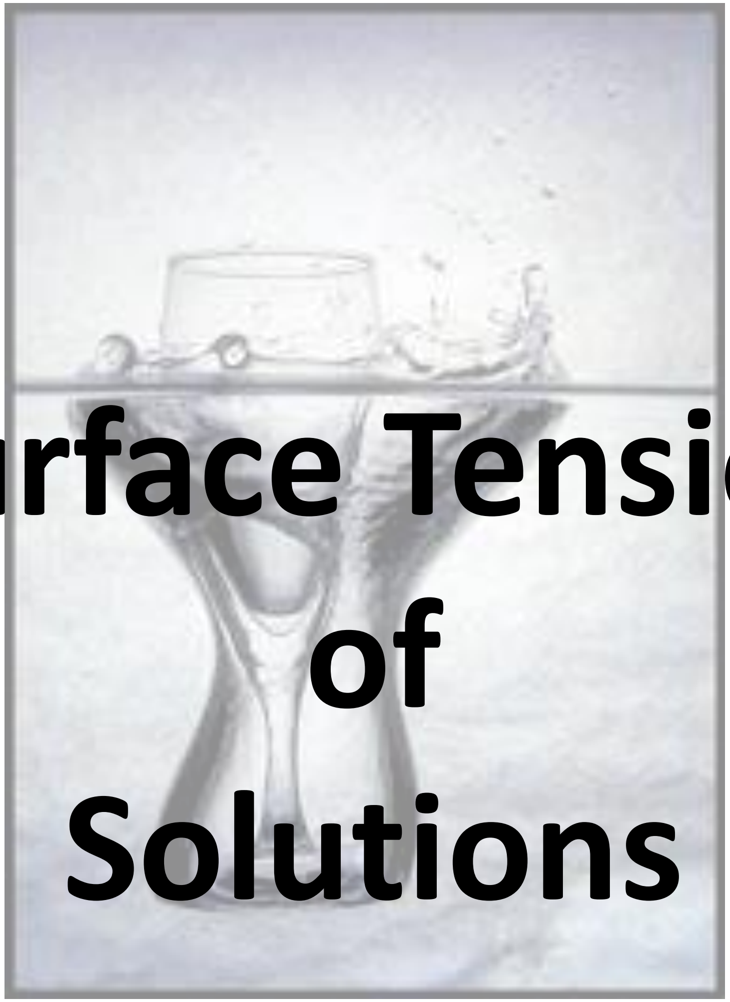

Surface Tension of Solutions

Picturepost.wordpress.com

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(or by appointment)

Purpose

- Measure the capillary rise of aqueous *iso*-butanol solutions at various concentrations.
- Calculate the surface tension of the solutions as a function of their *iso*-butanol concentrations.
- Use graphical analysis to determine the excess surface concentration of *iso*-butanol.

Theory

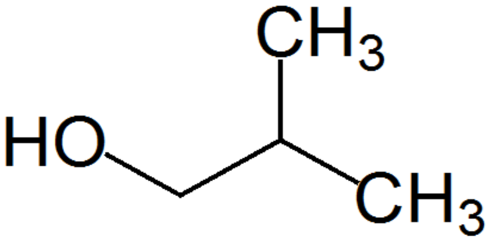
- Surface tension (γ) is the reversible work needed per unit area to form a surface.

- Excess surface concentration (Γ) can be calculated from the surface tension of a solution via the capillary rise method.

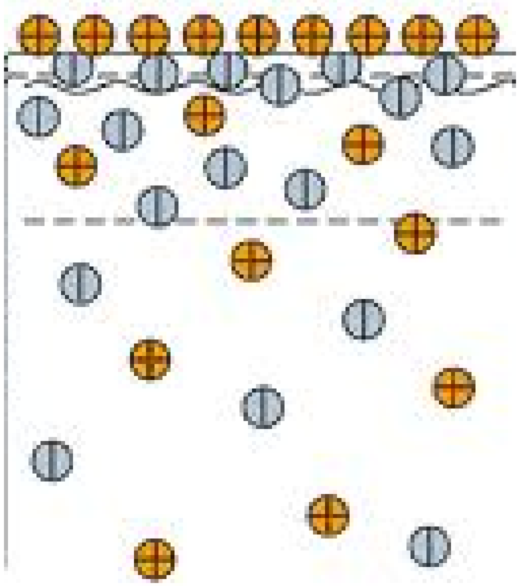
anniesbiozone.blogspot.com

Telegraph.co.uk

Iso-butanol



- It is easier to disrupt the intermolecular forces that exist between iso-butanol molecules than between water molecules.
- Therefore:
  - there is an excess of solute molecules at the surface.
  - the surface tension of a butanol solution is lower than that of water.



Brookhaveninstruments.com

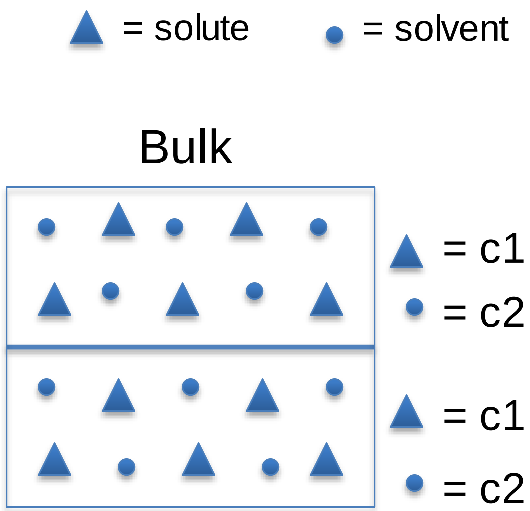
Surface Tension ➔ Surface Concentration

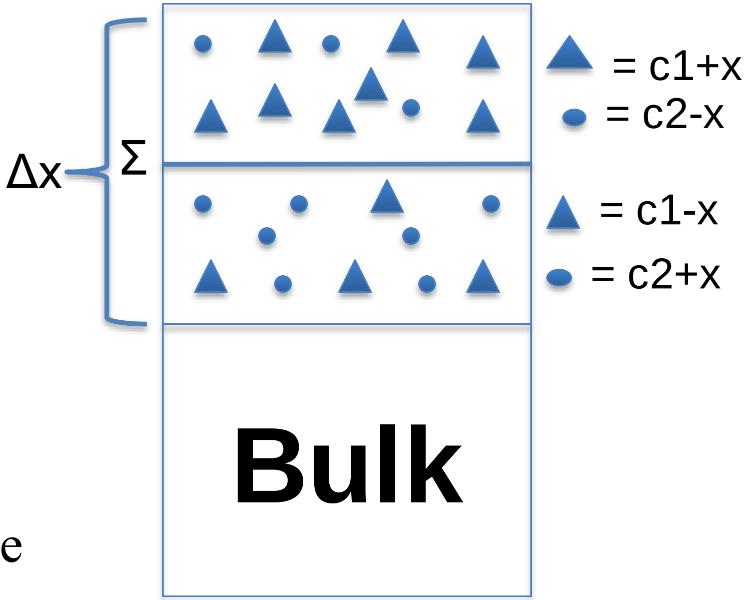
- Under constant *T* and *P*, a system will reach an equilibrium state with the lowest free energy, *G*. A liquid with a free surface will assume the shape that gives it the lowest *G*; this shape is dependent on the surface tension.
- Solutions generally have different surface tensions than pure solvents.
  - Particles of solutes that cause a decrease in surface tension tend to concentrate slightly near the surface; the opposite is true for solutes that increase the surface tension.
  - The movement of solute particles lowers the surface tension, and thus *G*, of the solution.
- Determination of the surface tensions over a variety of concentrations allows for the calculation of the excess surface concentration through the use of the Gibbs Isotherm.

$$\Gamma = \frac{-1}{RT}\frac{d\gamma}{d\ln[a_x]}$$

Where:
Γ = excess surface concentration
R = gas constant
T = temperature
γ = surface tension
a = activity
* Assumes a linear trend

- Bulk solution
  - If an arbitrary line is drawn, the concentration of solute and solvent above the line will equal the amount below the line.
- Γ for a solution where γ solute < γ solvent:
  - A gradient (Δx) exists at the top of the solution.
  - As we approach the surface the amount of solute increases and displaces the solvent, resulting in a decrease of the solvent.
  - An imaginary line (Σ) can be drawn such that the number of molecules of solvent depleted (c-w) above the line (due to displacement by the solute) is equal to the number added (c+w) below the line.
  - Since above this line the solvent is being displaced by the solute, the amount of solute increases above the line.

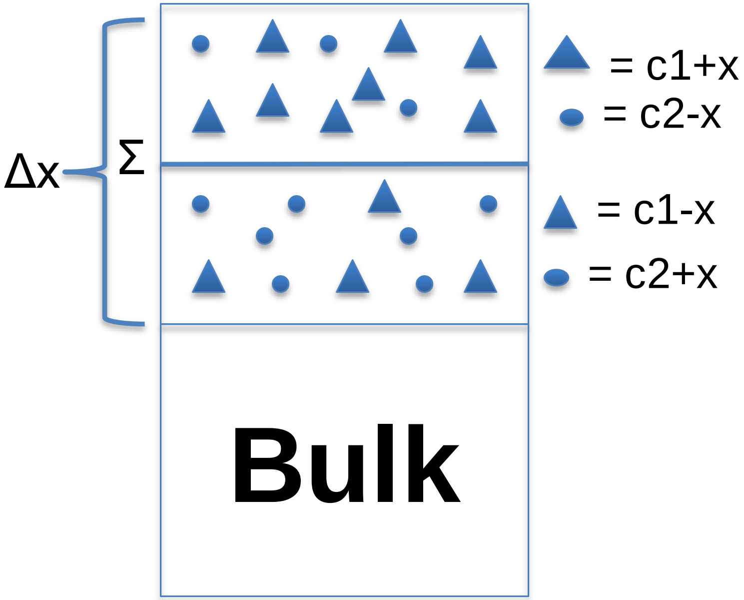




When Δx approaches zero, solvent molecules diminish and solute molecules become prominent

When a single molecule thick layer of solute molecules completely occupies the top surface of the system, it is said to be a monolayer packing

Surface excess concentration can be used to estimate whether a monolayer is formed or not as it gives the number molecules with a region of interest.

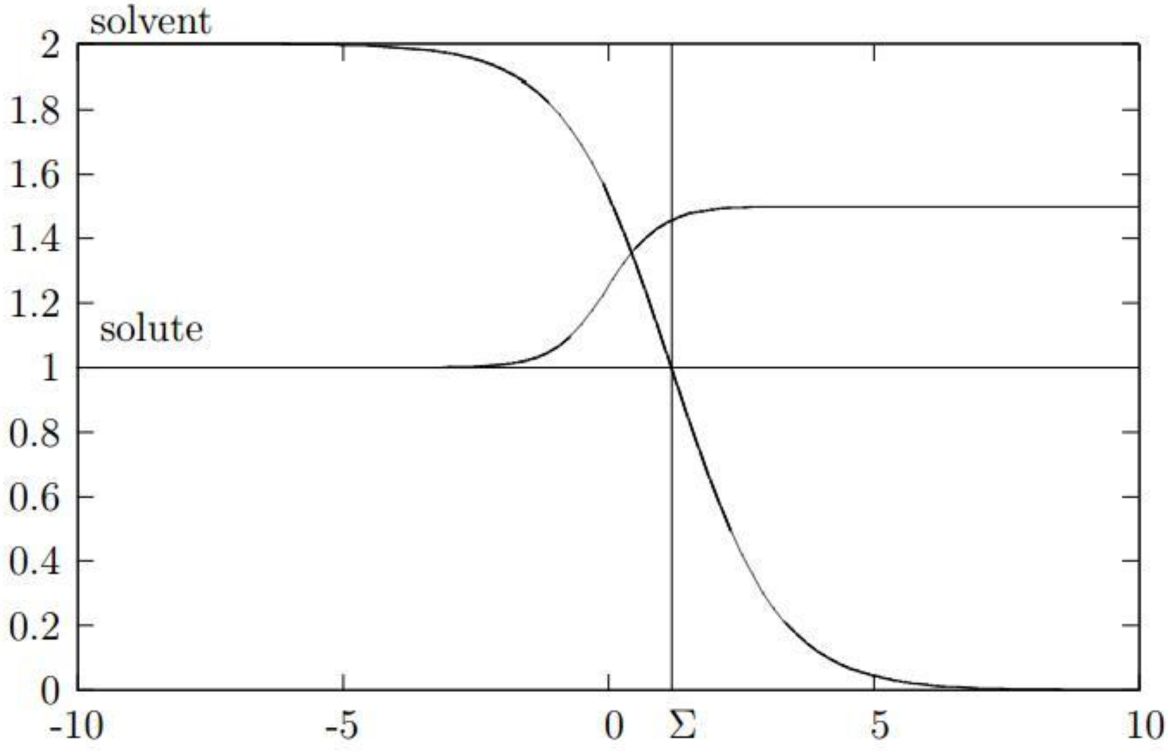


Theory

-To the right is another example of how the imaginary line, Σ, is chosen when γ solute < γ solvent

-The number of mols of solvent to the right of Σ is equal to the deficit number of mols of solvent to the left of Σ, such that the excess number of mols of solvent is equal to 0.

- For the solute, the number of mols on the right of Σ is not equal to the deficit of mols to the left and therefore is in excess.



Capillary Rise Method

- If the surface tension of a liquid which is in contact with a solid is . . .
  - Lower, it will wet the surface
  - Higher, it will avoid the surface

. . . in order to minimize the free energy of the system.

- Because the liquid surface is curved, there exists a pressure difference across the gas-liquid interface in the capillary.
- This pressure difference is balanced by the pull of gravity on the liquid in the capillary.

$$\Delta P = 2\gamma/r = \rho g h$$

- Therefore,

$$h = 2\gamma/\rho g r \ *$$

Where:
P = pressure
γ = surface tension
r = radius of the capillary
ρ = density
g = acceleration due to gravity
h = height of capillary rise
* Assumes a contact angle of 0°

Engel, T.; Reid, P. *Thermodynamics, Statistical Thermodynamics, & Kinetics;* Pearson: Boston, 2006, p184.

Procedure

Record the temperature of the bath, then perform this procedure on water and the following *iso*-butanol dilutions in order:

5mL/50mL, 15mL/50mL, 25mL/50mL, 35mL/50mL, and the 0.80 M stock solution (Exact concentration and the error of the stock solution is given on label of the bottle).

1) Rinse the test tube & capillary with solution.
2) Pour the remainder of the solution into the test tube. Replace the stopper. The solution level on the outside must be between 0.005 and 0.01 on the capillary.
3) Squeeze the rubber bulb, place it on the end of the capillary, and watch the meniscus while releasing the bulb (meniscus should rise). Remove the bulb (meniscus should drop).

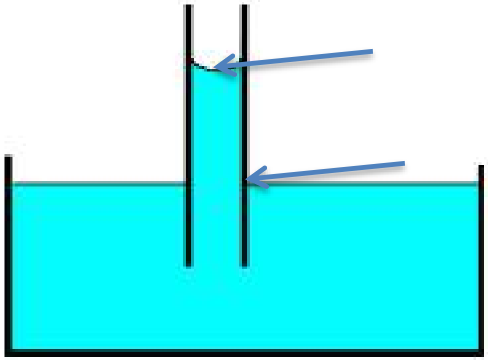
Procedure Continued

4) Record the final resting position of the meniscus and the level of the liquid in the test tube. For this experiment, units of height are unimportant owing to the use of ratios.

5) Repeat these measurements 5 times.

6) Clean the capillary with water between solutions and rinse with the next solution; dry it by forcing air through the capillary using the air jets.

*Remember to record the error in the stock solution and all volumetric glassware used for dilutions.



epa.gov

Notes on Procedure

- Be sure to dry the capillary thoroughly after cleaning with water between each solution.

- Beware of bubbles in the capillary during measurements.
  - To clear bubbles, place the bulb directly on the capillary and draw liquid out the top of the capillary.
  - Notify TA if bubbles remain.

- **Don’t forget to record the bath temperature.**

Data Analysis

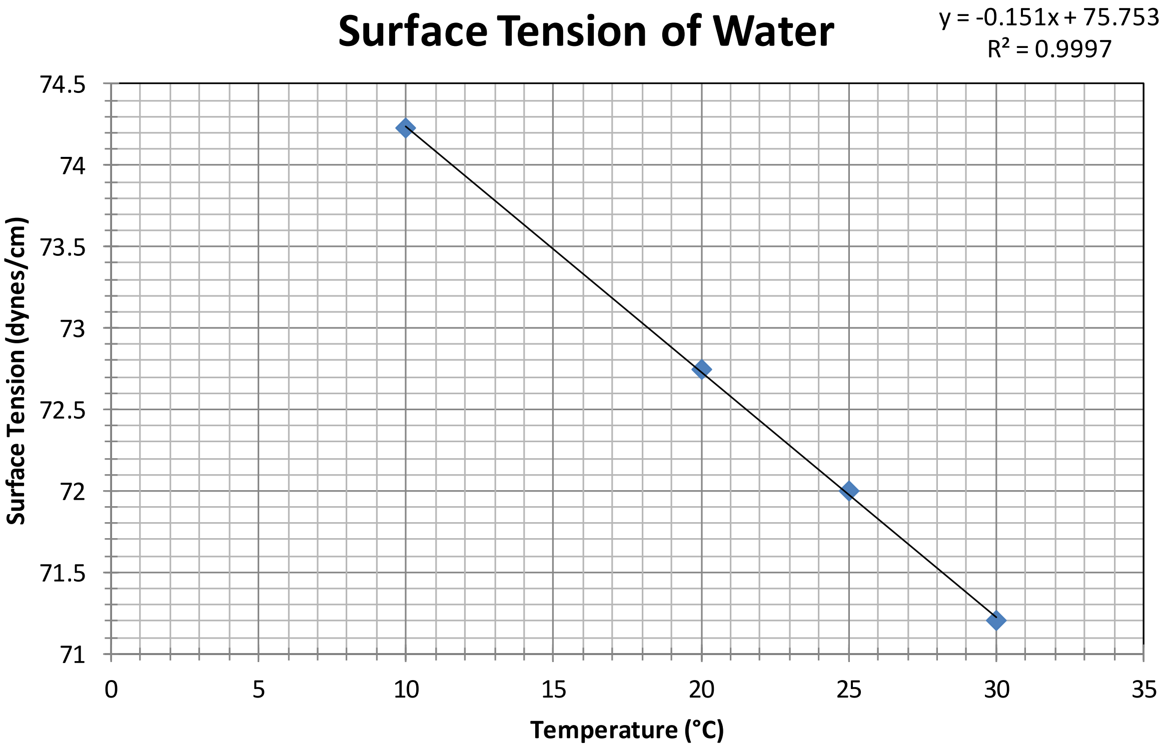
1. Surface Tension: The difference in height (h = meniscus height – solution height) is proportional to the surface tension (γ).*

Therefore:

$$\frac{h_{soln}}{h_{water}} = \frac{\gamma_{soln}}{\gamma_{water}}$$

*This proportionality is possible because the radius, *r*, is constant. The contact angle is also assumed to be constant.

1 dyne/cm = 0.01 J/m²



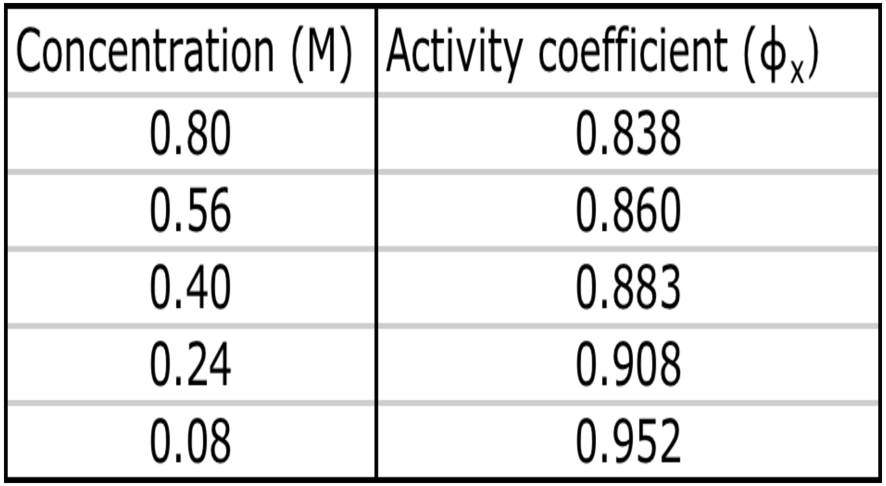
Use this chart to determine the surface tension of water at the appropriate T, then use the proportionality above to calculate surface tension.

2. Activity: Activity (*a*) is the “effective concentration” of a solution.

$$a_x = [X]\phi_x$$

Where:
$[X]$ = concentration
ϕ_x = activity coefficient

Use the following values of ϕ_x to calculate the activity of the butanol solutions:



Concentration (M)	Activity coefficient (ϕ_x)
0.80	0.838
0.56	0.860
0.40	0.883
0.24	0.908
0.08	0.952

1.) Skoog, West, Holler, Crouch. Fundamentals of Analytical Chemistry, Eighth Edition.

3. Plot surface tension as a function of the natural log (ln) of activity of each solution. Draw a line of best fit and determine the slope of that line. Assume the trend is linear for the given range of solutions.

3. Excess Surface Concentration: Calculate the excess surface concentration (in mol m^{-2} and molecules $Å^{-2}$) using the Gibbs isotherm,

$$\Gamma = \frac{-1}{RT}\overbrace{\frac{d\gamma}{d\ln[a_x]}}^{\textbf{Slope}} = \frac{-1}{RT}(Slope)$$

where R is the ideal gas constant (8.3144 J mol^{-1} K^{-1}), T is the average temperature in Kelvin, and a is the activity of the solution.

Error Analysis

1. Calculate $2\sigma_N$ for the capillary rise of each solution. If $2\sigma_N$ is zero, use 0.0001 as your error on the graph and in any future calculations.
2. Determine the error in activity and surface tension for the first and last data point on the graph of surface tension vs. ln activity.
   - Remember to record the error in the stock solution and in the pipettes and volumetric flasks that were used for each dilution.
   - Assume that the surface tension of water and the activity coefficient have no error.
   - Use the multiplication/division cookie cutter model for the proportionality.
3. Draw error boxes and use them to determine the error in the excess surface concentration (ie error in the slope) via the method of limiting slopes.
   - Assuming that the error in T is negligible and there is no error in R.

Lab Report

- Cover Page – Title, Date, Your Name, Lab Partner
- Abstract – What you did, why & how you did it, and your primary results plus associated error.
- Introduction – Purpose of the experiment
- Theory – Using complete sentences & your own words, describe surface tension & excess surface concentration, and explain the connection between the two. Make sure to define all variables for any equations used. NO DERIVATION REQUIRED!!!
- Procedure & Original Data – Signed by TA
- Calculations – Show all work
- Graphical Analysis – Hand drawn plot with appropriate labels
- Error Analysis – Propagation of errors, both mathematically and graphically; show all work
- Summary of Data – Final table with all results and corresponding errors
- Conclusions – See discussion information on the following slide

Discussion

1. Discuss the trend seen in the graph of surface tension vs. ln activity. Does this trend make sense for butanol solutions given that activity is proportional to concentration? Explain.
2. Use the following bond lengths[*] to estimate the length of an iso-butanol molecule.

C-H	1.09 Å
C-C	1.54 Å
O-H	0.96 Å
C-O	1.43 Å

3. Use the calculated excess surface concentration in molecules per Å^2 to estimate the average length, in Å, of a butanol molecule. Based on this answer and the value calculated in question #2, is a monolayer a good description of the surface layer of these solutions? Discuss the reasons behind your answer.

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[*] Wikipedia