Surface Tension of Liquids

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Office Hours Tuesdays 11 am
DuNouy Tensiometer Method

- Study of the change in **Surface Tension** as a function of concentration for different alcohols in water
- The data are interpreted in terms of the surface concentration using the **Gibbs isotherm**
Theory

Surface Concentration $\Gamma$

• Units of \textit{moles/m}^2\textit{or molecules/Å}^2

• \textbf{Bulk Concentration} $\Rightarrow$ concentration in the interior of solutions

• \textbf{Surface Concentration $\Gamma$} $\Rightarrow$ It represents excess of solute per unit area of the surface over what would be present if the bulk concentration prevailed all the way to the surface
Theory

Surface Tension $\gamma$

To break or change the shape or area of a surface it is necessary to do work. This work counterbalances the resistance the surface is offering to the change. The work per unit area is called the surface tension.

The surface tension of a surface represents the amount of work necessary to be applied on the surface in order for this to change its shape (break, stretch)

Units of $N\cdot m^{-1}$ or $J/m^2$
Theory

The Gibss Isotherm
Surface Concentration $\Gamma$ of Solutions

\[
\frac{\Gamma}{a} = -\frac{1}{RT} \frac{d\gamma}{da} \quad (1)
\]
\[
a = c \sigma \quad (2)
\]

where $\sigma$ is the activity coefficient

(1) can be written as:

\[
\Gamma = -\frac{1}{RT} \frac{d\gamma}{d(\ln a)} = -\frac{1}{2.303RT} \frac{d\gamma}{d(\log_{10} a)} \quad (3)
\]
Theory

Surface Active Substances
Surface Adsorption

- Many organic solutes, especially polar molecules, considerably reduce the surface tension of water.

- Such solutes tend to accumulate strongly at the surface, where in many cases they form a unimolecular film of adsorbed molecules.
Theory

Surface Active Substances
Surface Adsorption

• When this film is complete can’t accept anymore molecules
• As a consequence, the surface concentration undergoes little change when the bulk concentration is increased further over a wide range
  ▪ This behavior is depicted by

  The Gibbs Isotherm

  \[ \Gamma = \frac{-1}{RT} \frac{d\gamma}{d(\ln a)} = \frac{-1}{2.303 \cdot RT} \frac{d\gamma}{d(\log_{10} a)} \]

  \( (3) \)
Theory

The Gibbs Isotherm
See Figure 1

A plot of the surface tension $\gamma$ of the solution against the log of the activity will be linear over a range of concentration
Experimental Set Up

DuNouy Tensiometer Method
The Ring Method

Measure of the work per unit area necessary to pull a metal ring free from the surface of a liquid \( \Rightarrow \text{Surface Tension} \ \gamma \)

- The ring is hung from the beam of a torsion balance
- Set the balance to zero (mark in the mirror leveled with arm)
- Ring must be immersed completely in the liquid, just underneath the meniscus
- Turn knob on the right and knob at the base so that the mark on the mirror remained level
- Read off measurement when surface breaks.
Experimental Set Up

Calibration with water: Correction Factor

• It is necessary to apply a correction factor that takes into account the shape of the liquid held up by the ring (the ring is not perfectly flat and circular. It is bent and tilted. The liquid film (surface) will not be perfectly flat and some liquid will flow downwards, making the surface tension not even over the surface.

• We calibrate by measuring $\gamma$ for water.
• Take 5 measurements and take the average to be $\gamma$.
• The correction factor will be $[72.0/\gamma]$, where 72.0 dyn/cm is the literature value of surface tension of water and $\gamma$ is the experimental value.

• Multiply every future measurements by this correction factor.
Apparatus

Experimental Set Up

DuNouy Tensiometer

Method

The Ring Method
Procedure

DuNouy Tensiometer Method

The Ring Method

• Make sure the dial of the tensiometer is set to zero before making any adjustment

• First, a calibration of the tensiometer is performed measuring $\gamma$ for distilled water. The tabulated value is 72 dy/cm$^{-1}$

• $\gamma$ for distilled water read on the instrument may differed significantly from 72 dy/cm$^{-1}$

• Correct every reading by a factor of $[72/ \gamma]$ where $\gamma$ is the surface tension of distilled water obtained from the instrumental measurement
DuNouy Tensiometer Method
The Ring Method

- Repeat the measurement of $\gamma$ for distilled water 4 times
- Record temperature of the room once (Thermometer in barometer)
- On the stock solution provided by TA measure $\gamma$. Dilute to precisely three quarters the concentration and repeat measurement and so on until eight concentrations have been used. Last concentration should be $\sim 0.11$M
• DuNouy Tensiometer Method
  The Ring Method
• Take three readings for each concentration
• Multiply every reading by the correction factor $\left[\frac{72}{\gamma}\right]$
• You are going to use approximately 50ml of every solution in each measurement. Don’t discard after measuring. Use it for next dilution
• Rinse pipettes with a small volume of the solution to measure
• Wipe and dry ring in between measurements. The ring must be clean and dry for each new solution
• Use a chemwipe to touch ring
• You are not to perform the NaCl experiment
• Rinse ring with distilled water when finish and dispose of the waste as directed by TA
Calculations of the Solutions

- **solution 1** ⇒ Stock Solution 0.8 M
- **Solution 2** concentration will be ⇒ 0.6M
- **Solution 3** concentration will be ⇒ 0.45M
- **Solution 4** ⇒ 0.45V_i=3/4(0.45)100ml ⇒ 0.34M
- **Solution 5** ⇒ 0.34V_i=3/4(0.34)100ml ⇒ 0.25M
- **Solution 6** ⇒ 0.25V_i=3/4(0.25)100ml ⇒ 0.19M
- **Solution 7** ⇒ 0.19V_i=3/4(0.19)100ml ⇒ 0.14M
- **Solution 8** ⇒ 0.14V_i=3/4(0.14)100ml ⇒ 0.11M

- Assuming 100 ml is the final volume of each new solution, a dilution of ¾ means to take 75ml of the previous solution and diluted to 100 ml.
Calculations

- Calculate surface concentration $\Gamma$ in both units of $\text{mol/cm}^2$ and $\text{molecules/Å}^2$
- For the alcohol solutions, use extrapolated activity coefficients in (3)

$$\Gamma = -[1/RT] \frac{d\gamma}{d(\ln a)} = -[1/2.303RT] \frac{d\gamma}{d(\log_{10}a)} \tag{3}$$

$$d\gamma = -\Gamma RT \, d\ln a \tag{4}$$

where $a$ is the activity of the solute

The activity is equals to the concentration of the solute times the activity coefficients

Use the extrapolated values of activity coefficients given in the textbook

(pg 294 footnote)
Calculations and Error Analysis

Calibration of Tensiometer: Calibration Factor

• Report $\gamma$ taken for water
• Calculate **Correction Factor** and report the value using the correct number of significant figures
• Show calculation of the error in the correction factor
• Report Temperature with significant figures and error
Calculations and Error Analysis

- Propagate the error $\varepsilon(\Gamma)$ for only the first and last point on the plot.

\[ \Gamma = -\frac{1}{RT} \frac{d\gamma}{d\ln a} = -\frac{1}{2.303RT} \frac{d\gamma}{d\log_{10} a} \]  

\[ \varepsilon(\Gamma) = \left[ \frac{\partial \Gamma}{\partial \gamma} \right] a \varepsilon(\gamma) + \left[ \frac{\partial \Gamma}{\partial \ln a} \right] \gamma \varepsilon(\ln a) \]  

\[ \varepsilon(\Gamma)^2 = \left[ \frac{\partial \Gamma}{\partial \gamma} \right] a^2 \varepsilon(\gamma)^2 + \left[ \frac{\partial \Gamma}{\partial \ln a} \right] \gamma^2 \varepsilon(\ln a)^2 \]  

- Derive an expression for $\varepsilon(\Gamma)^2$ using (5).
- Show your derivations.
- Derive an expression for $\varepsilon(\gamma)$ and $\varepsilon(\ln a)$. 
Calculations and Error Analysis

• Report all the necessary information needed for calculations

\[ C_0 = C_{\text{Stock}} = \frac{V_a}{V_f} \cdot d \cdot 1000 / MW = b \cdot \frac{V_a}{V_f} \]

\[ b = d \cdot 1000 / MW \]

\[ V_a = \text{Volume of alcohol taken to prepare Stock Solution} \]

\[ V_f = \text{Final Volume (Volume of Volumetric Flask)} \]

Report \( \varepsilon(V_a) \) and \( \varepsilon(V_f) \) [Hint: errors in volumetric pipettes and flasks: look in the lab handout for pipettes and in the flask in the lab for each flask]
Calculations and Error Analysis

• Show a formula showing how to calculate the concentration resulting after dilution from the stock solution [Hint: use the previous concentration, the volume taken of the previous solution and the final volume of the new solution]

• Show a formula for finding $\varepsilon(c)$ where $c$ is the new concentration after dilution [Hint: propagation of expression such as $xy/z$]
Error Analysis

- Plot the experimental surface tension of the solution $\gamma$ against the log of the activity of the solution.

- Calculate $\varepsilon(\Gamma)$ using only the first and last points on the graph.

- Use the two calculated errors to determine the limiting slopes of your graph as explained in lab handout pg 28.

- Use the limiting slopes to estimate the error in your determined surface concentration.
Error Analysis

- Express $\Gamma \pm \varepsilon(\Gamma)$ in units of mol/m$^2$ and molecules/Å$^2$. Show how you obtained this units [Hint: equation 3, Avogadro number]
Presentation of Data

• Attach chart showing concentration, surface tension read off from tensiometer [reported as $[\gamma \pm \varepsilon(\gamma)]$] and corrected values for each solution numbered from the stock solution to the last taken. Each value must present its significant figures, error and units if applicable.

• Attach chart showing solution number, $[c \pm \varepsilon(c)]$, activity coefficient $[(a_c) \pm \varepsilon(a_c)]$, $[\ln(a) \pm \varepsilon(a)]$, corrected $[\gamma \pm \varepsilon(\gamma)]$
Presentation of Data

• Must show calculations concerning the measured average value for surface tension of water, discussion of its significant figures, correction factor and its significant figures.
Presentation of Data

• Must show calculation of concentration and activities used with their significant figures
• Must include derivation of formulas for error analysis
Conclusions

• Discuss the magnitude of the surface concentration

• Discussion of other form of errors rather than statistical affecting this experiment (systematic errors)
Lab Report

- **Cover Page**: title, date lab was performed and name of lab partner
- **Abstract**: summary of the lab experiment including results
- **Introduction**: discussion of the purpose of the experiment
- **Theory**: derivation of key formulas in the experiment
- **Procedure**: signed by TA
- **Data**: originally set up sheet signed by TA
- **Results**: Data in chart as explained above to be used for calculations
- **Calculations**: provide sample calculations. Important
Lab Report

• **Error Analysis**: as explained above
• **Summary**: final results with errors, proper units and significant figures
• **Conclusions**