Measuring Surface Tensions for Solvents in ESI Mass Spectrometry

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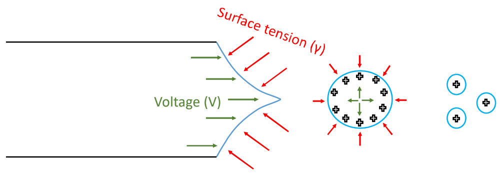
Background & Instrumentation

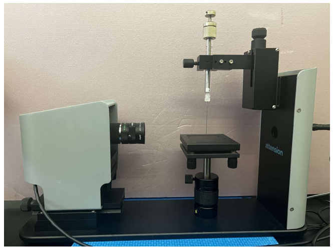
In electrospray ionization mass spectrometry samples are analyzed via ejection and vaporization from a capillary. When the solvent containing the sample is ejected from the emitter tip it forms droplets that are then vaporized. The surface tension of the solvent used is an important part of this process. By using lower surface tension solvents, smaller droplets are formed that are more easily evaporated.



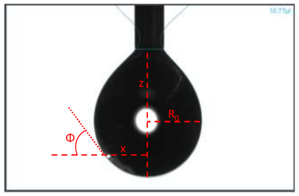
$$E_0(r_c) = \left[\frac{2\gamma\cos(\theta_0)}{\epsilon_0 r_c}\right]^{\frac{1}{2}}$$

$$V_0 = 0.5\left[\frac{2\gamma r_c\cos(\theta_0)}{\epsilon_0}\right]^{\frac{1}{2}}\ln\left(\frac{4h}{r_c}\right)$$

These equations use the dimensions of the emitter tip, ($\mathbf{r_c}$, $\mathbf{h}$, $\boldsymbol{\theta_0}$) to relate surface tension ($\boldsymbol{\gamma}$) to the onset voltage ($\mathbf{V_0}$) and electric field ($\mathbf{E_0}$).[1] The goal of our project was to examine the effects of solutes on surface tension. This work was done using a *Biolin Scientific* ThetaLite 100 tensiometer.



This instrument optically measures the surface tension of a liquid sample using a high zoom camera. Based on the density ($\boldsymbol{\rho}$) of the solution and geometry ($\boldsymbol{\beta}$) of a droplet the surface tension ($\boldsymbol{\gamma}$) is calculated. $\mathbf{R_0}$ describes the radius of the drop at the apex of curvature. The software uses the Young-Laplace method to estimate dimensions of the droplet where $\boldsymbol{\beta}$ is a combination of 3 equations.[2]



$$\gamma = \frac{\Delta\rho g R_0}{\beta}$$

$$\frac{dx}{ds} = \cos(\theta)$$

$$\frac{dz}{ds} = \sin(\theta)$$

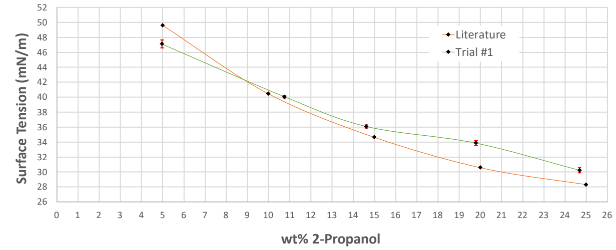
$$\frac{d\theta}{ds} = 2 + \beta z - \frac{\sin(\theta)}{x}$$

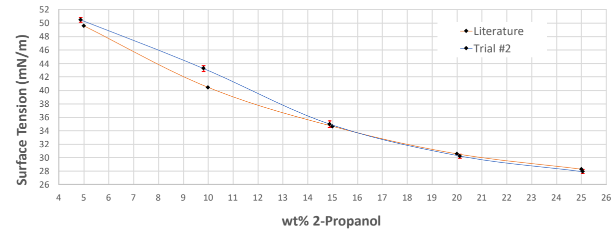
Data Collection

The first samples examined with the tensiometer were in comparison to literature values for solutions of 2-propanol and water. The goal was to make sure the instrument was capable of measuring mixed solutions and all parts worked properly. For future measurements this would help identify sources of error and how we might eliminate them.

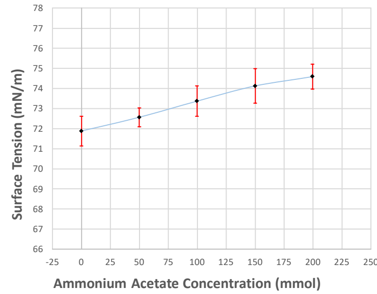
The second part of this experiment was taking varying concentrations of ammonium acetate aqueous solutions and measuring the surface tension using the previous methods.

Calibration Using Literature Values of Propanol





Ammonium Acetate Concentration vs. ST



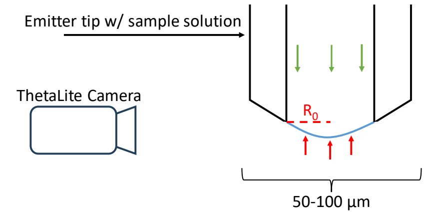
- Each data point averaged from 760 analyzed frames
- Error bars result from changes between each frame
- High deviation due to vibrations and evaporation of solvent (±0.6-0.8 mN/m)
- Future goal to reduce error below ±0.2 mN/m

Results

- Capable of measuring solution mixtures if density and composition were known
- Consistent temperature and humidity for all measurements resulted in more accurate data
- Linear relationship between molarity and surface tension for ammonium acetate ($R^2 = 0.993$)
- Samples that evaporated quickly had error between each frame between ±0.2-0.5 mN/m
- Instrument is highly sensitive to vibrations and air current, experiments best performed in isolated area
- Lower salt concertation would be better for achieving smaller spray droplets

Future Experiments

- Measuring surface tension of more dilute samples for notable changes
- Testing accuracy for low boiling point solvents & developing method of measurement
- Measuring more complicated solvent mixtures with differing polarity
- Compare data directly to mass spectra from same samples to see effects of concentration
- Using emitter tip directly in the ThetaLite100



References

[1] Smith, D. *IEEE Transactions on Industry Applications* **1986,** 529-529 10.1109/TIA.1986.4504754.

[2] *Biolin Scientific* Instrument Handbook: Surface Tension Measurement with Optical Tensiometer

[3] Vazquez, G.; Alvarez, E.; Navaza, J. M. *Journal of Chemical & Engineering Data* **1995**, *40* (3), 611–614. DOI:10.1021/je00019a016.

[4] Šamalikova, M.; Grandori, R. *Journal of Mass Spectrometry* **2005**, *40* (4), 503–510. DOI:10.1002/jms.821.