# Nano Spinning Things

## How the stuff works

# *Making Solutions*

## PHOSPHATE SOLUTION

### Chemicals & Equipment

- 1-Ethyl-3-methylimidazolium diethyl phosphate (Ionic Liquid)
- Dimethyl sulfoxide (DMSO)
- α-cellulose

- 100 ml beaker (maybe two)
- one of the magnet pill things to mix (or just a spatula)
- 2x 5-10ml measuring cylinders or 2.5-5ml syringes
- sometimes a weighing boat
- spatula

- (when the DMSO is solid, place some on a hot plate to melt)

1. Mix ionic liquid and DMSO, as to the required ratio (IL:DMSO)
2. Add and mix the cellulose, as to the required percentage by mass

**RECORD**

- volume of IL and DMSO
- mass of solution
- time and date @ end of making solution
- % of cellulose
- time mixed for
- power of the mixer (fraction of dial)
- temperature @ end of making solution
- humidity @ end of making solution
- Code → see spreadsheet

2.5% cellulose seems to be optimal (based on information from sieran,and original information from Penn)
above 5% is too viscous to spin

Mixing for 10-15 mins seems optimal, further experimentation needs to be done.

When older, phosphate solutions are recognizable by a cloudy green colour.

The solutions get more viscous over time, and so have a limited life span.

# Risk Assessment

## Needle Injuries

Could pierce skin, and also transfer chemicals.
Use needle caps, don't have exposed needles where not necessary.

## Chemical Injuries

For chemicals see linked safety data sheets

**1-Ethyl-3-methylimidazolium diethyl phosphate**
https://www.fishersci.com/store/msds?partNumber=AAH2740014&productDescription=1-ETHL-3-METHLIMIDAZOLIUM+25G&vendorId=VN00024248&countryCode=US&language=en

- Harmful if swallowed
- Can cause skin burns and eye damage
- May cause respiratory irritation
- If consumed, in eyes or inhaled, call poison center, first aid as normal
- If on skin, rinse skin with water thoroughly
- Don’t breathe directly in

**Dimethyl sulfoxide**
https://www.fishersci.co.uk/chemicalProductData_uk/wercs?itemCode=D/4120/21

- Not hazardous
- Can penetrate skin, can carry dissolved chemicals
- If consumed, in eyes or inhaled, first aid as normal
- If on skin, wash with soap and water for 15 mins immediately

**α-cellulose**
https://www.cellucomp.com/uploads/tinymce/MSDS%20-%20Curran.pdf

- Not hazardous
- If consumed, in eyes or inhaled, first aid as normal
- If on skin, wash with soap and water

**General Prevention**

- Wear goggles

## Burning

Hot plate could cause burns if touched when hot.
Don’t touch when the hot plate is on, Inform people in the room when turning it on.

# ACETATE SOLUTION

## Chemicals & Equipment

- 1-Ethyl-3-methylimidazolium acetate (Ionic Liquid)
- Dimethyl sulfoxide (DMSO)
- α-cellulose

- 100 ml beaker (maybe two)
- one of the magnet pill things to mix (or just a spatula)
- 2x 5-10ml measuring cylinders or 2.5-5ml syringes
- sometimes a weighing boat
- spatula

- (when the DMSO is solid, place some on a hot plate to melt)

1. Mix ionic liquid and DMSO, as to the required ratio (IL:DMSO)
2. Add and mix the cellulose, as to the required percentage by mass

**RECORD**

- volume of IL and DMSO
- mass of solution
- time and date @ end of making solution
- % of cellulose
- time mixed for
- power of the mixer (fraction of dial)
- temperature @ end of making solution
- humidity @ end of making solution
- Code → see spreadsheet

2.5% cellulose seems to be optimal (based on information from sieran,and original information from Penn)
above 5% is too viscous to spin

Mixing for 10-15 mins seems optimal, further experimentation needs to be done.

when older, acetate solutions are recognizable by a cloudy orange colour

## Risk Assessment

### Needle Injuries

Could pierce skin, and also transfer chemicals.
Use needle caps, don't have exposed needles where not necessary.

### Chemical Injuries

For chemicals see linked safety data sheets

**1-Ethyl-3-methylimidazolium acetate**
https://iolitec.de/sites/iolitec.de/files/sds/SDS%20IL-0189%20EMIM%20OAc%2C%201-Ethyl-3-methylimidazolium%20acetate.pdf

- Not hazardous
- If consumed, in eyes or inhaled, first aid as normal
- If on skin, wash with soap and water

**Dimethyl sulfoxide**
https://www.fishersci.co.uk/chemicalProductData_uk/wercs?itemCode=D/4120/21

- Not hazardous
- Can penetrate skin, can carry dissolved chemicals
- If consumed, in eyes or inhaled, first aid as normal
- If on skin, wash with soap and water for 15 mins immediately

**α-cellulose**
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- Not hazardous
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- If on skin, wash with soap and water

**General Prevention**

- Wear goggles

### Burning

Hot plate could cause burns if touched when hot.
Don't touch when the hot plate is on, Inform people in the room when turning it on.

# POLYOX SOLUTION

## Chemicals & Equipment

- Polyethylene oxide (polyox) with a molecular weight of <1M
- Distilled water

- 100 or 50 ml beaker
- one of the ma
- gnet pill things to mix
- weighing boat
- spatula

1. Measure mass of distilled water as to the required percentage by weight
2. Add the polyox, as to the required percentage by weight, slowly over time while mixing

Mix for a long time, at least 30 mins (we did 36 mins for a 1.6% solution) → currently investigating alternative methods

North Penn finds 8% @ 900K molecular weight to work best.

A note on molecular weight: We standardise 900K with North Penn, but also have some 4M available. Higher molecular weights will spin less reliably, and be very viscous

Update: We have found that using 4M polyox does work, just at very low solutions. North Penn suggested 1.5-2.5% and after parameter testing, we found that towards 1.5% works best. Use heat lamp.

## Risk Assessment

### Needle Injuries

Could pierce skin, and also transfer chemicals.
Use needle caps, don't have exposed needles where not necessary.

### Chemical Injuries

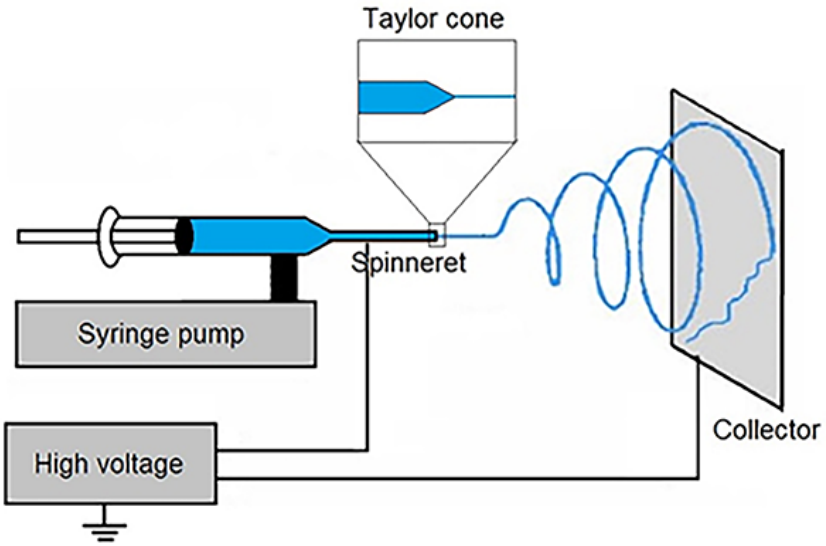
For chemicals see linked safety data sheets
**Polyethylene oxide**
https://www.fishersci.com/store/msds?partNumber=AC178580050&productDescription=POLY%28ETHYLENE+OXIDE%29+5G&vendorId=VN00032119&countryCode=US&language=en

- Not hazardous
- If consumed, in eyes or inhaled, first aid as normal
- If on skin, wash with soap and water

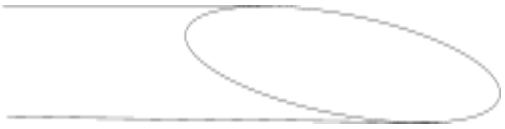
**General Prevention**

- Wear goggles

# *Electrospinning the Solutions*




- High voltage power supply
- Syringe pump
- Collecting plate/drum
- Syringe of solution
- Hypodermic needle (uniaxial spinneret) that is like the shape opposite



To spin, set up equipment in the diagram below, and note the variables below. (Use a data collection sheet if unsure of how to collect data, find them here or in the cupboard)

**RECORD**

- solution details
- solution code
- distance between needle and plate
- whether the aluminium foil is hexed or smooth
- acceleration voltage
- extrusion rate
- time left for
- date and time spun @ start
- humidity
- temperature
- mass of solution after
- mass of solution before
- change in mass of solution before spin from last recorded mass
- age (in days) for IL/Cellulose solutions

The most effective solution seems to be 1:1 2.5% acetate at 14 days old (+/- 4 days), provided it isn't too viscous.

Generally the most effective setup for spinning is 0.25ml/h, 5kV, 5cm (for cellulose solutions)

- The higher the acceleration voltage and lower the distance (within reason) results in a higher quantity of fibres, and a higher voltage will mean smaller fibres. As a very rough rule 1kV to 1cm.

We use a gauge of 19G to standardise with North Penn

We are currently investigating the use of 0.37 and 0.5 ml/h. 0.5 ml/h extrusion rate will result in fibres being produced more quickly, and is recommended for polyox

While spinning, the solution should form a taylor cone, before jumping to the plate, forming a fibre. If the taylor cone does not form and the solution either drops, or forms a long cylinder type thing, it isn't going to spin under the current setup.

When a cellulose fibre from the DMSO evaporates. You can seperate the ionic liquid and cellulose by washing the fibres in ethanol.

## TAKING SAMPLES

We are currently investigating better ways to sample the nanofibers.
Samples deteriorate over time.
Be sure not to contaminate samples, and for more success, have a high fiber density.

### Collector Plate

*Carefully*, swipe a clean slide between the needle and collection plate, if possible using insulated tongs. Leave the HV on, otherwise the fibres will fall and break. If using the SEM, then place the carbon onto the slide before, or place the carbon on the foil.

### Rotating Drum

For use with the SEM, place the carbon on the foil cover and align it with the needle. If not using the SEM for analysis, remove the foil.

## RISK ASSESSMENT

### Electric Shock

Touching the wires, needle or plate could result in an electric shock.
If set up incorrectly, touching the table could result in an electric shock.
Don't put voltage above 5 kV, make people aware the power supply is connected and on, place the screen in front of the spin setup, check the table is not charged using a voltmeter.

### Needle Injuries

Could pierce skin, and also transfer chemicals.

Use needle caps, don't have exposed needles where not necessary. Make people aware when the needle is exposed for spinning. Use screen in front of the spin setup. Ensure students are aware on how to safely handle needles.

### Chemical Injuries

See risk assessment for given solution
In addition, Use screen in front of the spin setup.

# Method Sheet For Electrospinning

1. Write in the lab book information including:
    a. Solution Code/Number (e.g. #00E)
    b. Solution Description (e.g. 1:1 2.5% Phosphate or 5% Polyox)
    c. Spin Conditions (e.g. 5kV, 7cm, 0.25 ml $h^{-1}$)
    d. If possible, humidity and temperature (e.g. 70%, 17°C)
    e. (Any extra conditions, anything different to usual write down)
    f. Start and end time (e.g. START: 13:22, END: 13:32) pls use 24h
    g. Start and end mass (e.g. START: 13.20g, END: 13.16g)
    h. Age (except for polyox) of the solution (e.g. Age = 2 days)
    i. Description of the spin (did it spin, drop down, form globules? if in doubt include as much info as possible)
2. Measure start mass and record end time
3. **Put on safety glasses when handling solutions without needle cap**
4. Remove needle cap carefully and remove excess air from syringe
5. Place in syringe pump, ensure the latch is on
6. Adjust the syringe pump to be ready to pump, i.e. move black thing to the back of the syringe.
7. **Place RED crocodile clip on the end of the needle closest to the conductive plate**
8. Measure distance between the tip of the needle and conductive plate
9. Turn the syringe pump on
10. **Turn the HV power supply on, making sure noone is touching the table, and inform others in the room that the HV power supply is on.**
11. **Place protective screen in front of the setup**
12. Check on the solution occasionally, record notes in lab book
13. **After some time, turn the HV power supply off**
14. Turn the syringe pump off
15. Remove syringe, wipe down needle with a paper towel
16. Add excess air back into the syringe
17. **Replace needle cap, at an angle to avoid stabbing yourself**
18. Measure end mass and record end time

# Key Safety Notices

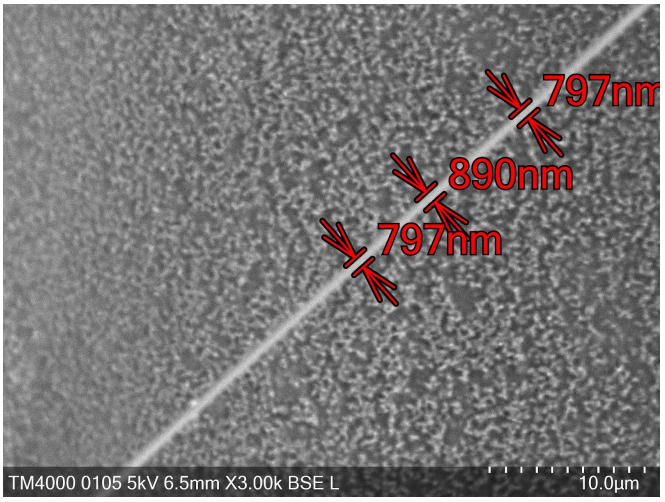
- Make sure the hv power supply is off before touching anything including the table
- Make sure the crocodile clip is connected before turning hv on
- Don't stab yourself
- Wash your hands well with soap if you are in contact with a solution
- **IF IN DOUBT, DON'T**

# *Scanning Electron Microscope Use*

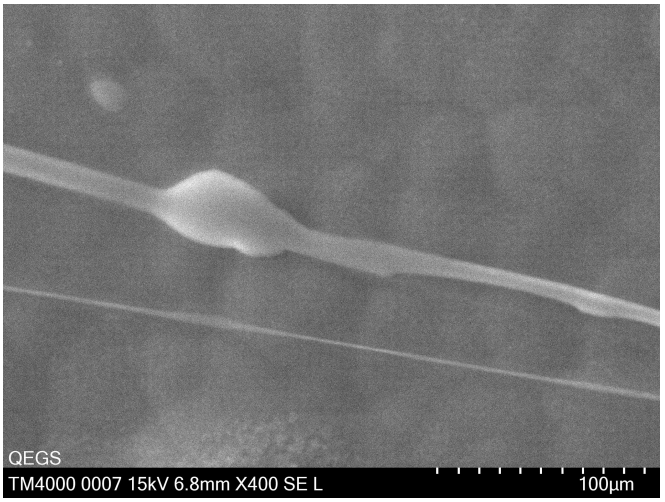
When using the electron microscope, you are looking for quite uniform fibres, maybe with some globule type things on them in some places. Be careful to not contaminate the sample. Use samples that have a high fibre density, so you can find them easily. Keep in mind that fibres on the $x10^{-9}$ scale will only be found on very large magnifications, at around x 3'000.

If you see beads form, then it is possible that the solution was not a high enough concentration of cellulose or polyox, or that the solution was too viscous to form a smooth fibre.

The best way to find nanofibres is to find microfibres with a high fibre density, and scan the edges of the fibre.




A nanofiber




A microfiber with an inconsistent diameter and a large bead

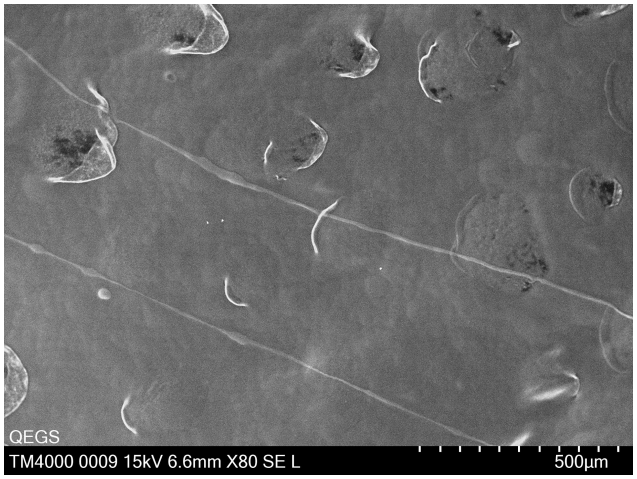
# *Current Projects for Ionic Liquid and Cellulose Solutions*

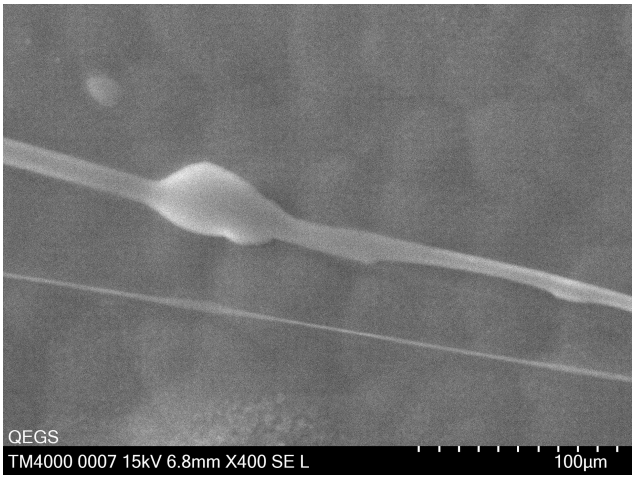
## ROTATING DRUM

- Look into using a rotating drum as a collection plate, to create properly aligned nanofibers for collection

We have successfully spun with the rotating drum, and found some successfully aligned microfibers under the SEM.

We still need to stabilise the movement of the drum so we can work out the optimal speed, and also ensure stable connectivity with the HV.




### In Future

We plan to redesign the drum using a slip ring and metal axle to better allow for connectivity in the drum, with better and more stable rotations.

Our plan is;

- to use a slip ring
- 3d print a frame that is more sturdy

## PRESERVING SAMPLES

- Look into a way to properly preserve and store nanofiber samples for analysis under the SEM

## KEEPING MARCUS IN THE LOOP

We need to send an email to Marcus at a regular interval with what we are doing, and also attach this doc as a pdf and the lab book scans. → Next email will be at the start of M2

### MEASURING THE TENSILE STRENGTH OF FIBRES

We could do this as a mesh and average out the strength quite easily, or we could send a sample to somewhere with an SEM that has a nanofactory.

### MEASURING VISCOSITY

We need to create a method to measure the viscosity of our solutions with a small volume. also same with resistivity, but that seems easier. We might need a capillary viscometer.

## *Complete Projects*

### AGEING

- Look into how the age of any solution affects its ability to spin, and the quality of spin

| | 1:1 2.5% acetate | 1:1 2.5% phosphate | 1:1 2.5% phosphate | 1:1 2.5% phosphate |
|---|---|---|---|---|
| 0 | N | N | X | Y |
| 1 | X | ~ | X | Y |
| 2 | Y | ~ | Y | Y |
| 3 | N | N | N | Y |
| 4 | N | N | Y | X |
| 5 | N | N | N | N |
| 6 | N | N | N | N |

| | |
|---|---|
| ~ | Kind of spun |
| X | Did not test |
| Y | Spun |
| N | Did not spin |

#### Preliminary

We have data for two runs between 0 and 6 weeks, a 1:1 2.5% acetate solution, and three 1:1 2.5% phosphate solutions. However, our earlier solutions were not spinning as much as we expected. Despite this our results are so far suggesting that 2 weeks is optimal for all solutions.

We believe that the phosphate solutions do better with some age, and all solutions decrease in effectiveness over time, as they congeal and become too viscous to spin.

Marcus says that one potential reason for the results is the fact cellulose is hydrophilic and so will absorb and move into water vapour in the air (which would make the solution more viscous over time). Thus, if we record the change in mass, we can work out the mass of water absorbed. Preliminary data on this suggests that this is true to some extent.

| Solution | #007 1:1 Phosphate 2.5% | | #009 1:1 Phosphate 2.5% | |
|---|---|---|---|---|
| Day Number | Spin | Δm (g) +/- 0.01 | Spin | Δm (g) +/- 0.01 |
| 0 | FALSE | 0 | FALSE | 0 |
| 1 | FALSE | ~ | FALSE | ~ |
| 2 | ~ | ~ | ~ | ~ |
| 3 | ~ | ~ | ~ | ~ |
| 4 | ~ | ~ | ~ | ~ |
| 5 | ~ | ~ | ~ | ~ |
| 6 | ~ | ~ | ~ | ~ |
| 7 | ~ | ~ | FALSE | 0.06 |
| 8 | FALSE | 0.74 | FALSE | -0.01 |
| 9 | FALSE | -0.01 | | |

## Method 1 (M1)

We are looking at how the age of solutions affects spin. M1 is testing if water gain could be responsible for the difference in ageing effects by spinning often.

All spinnable solutions within the ageing experiments are cellulose solutions, within M1 the only ionic liquid used was 1-Ethyl-3-methylimidazolium diethyl phosphate, as we do not currently have any 1-Ethyl-3-methylimidazolium acetate (which generally spins more reliably).

All ratios refer to Dimethyl sulfoxide : Ionic Liquid in that order without exception.

If our hypothesis is correct, we expect to see some overall mass gain, as the cellulose is hydrophilic and will absorb water vapour when humidity is high.

### Methodology

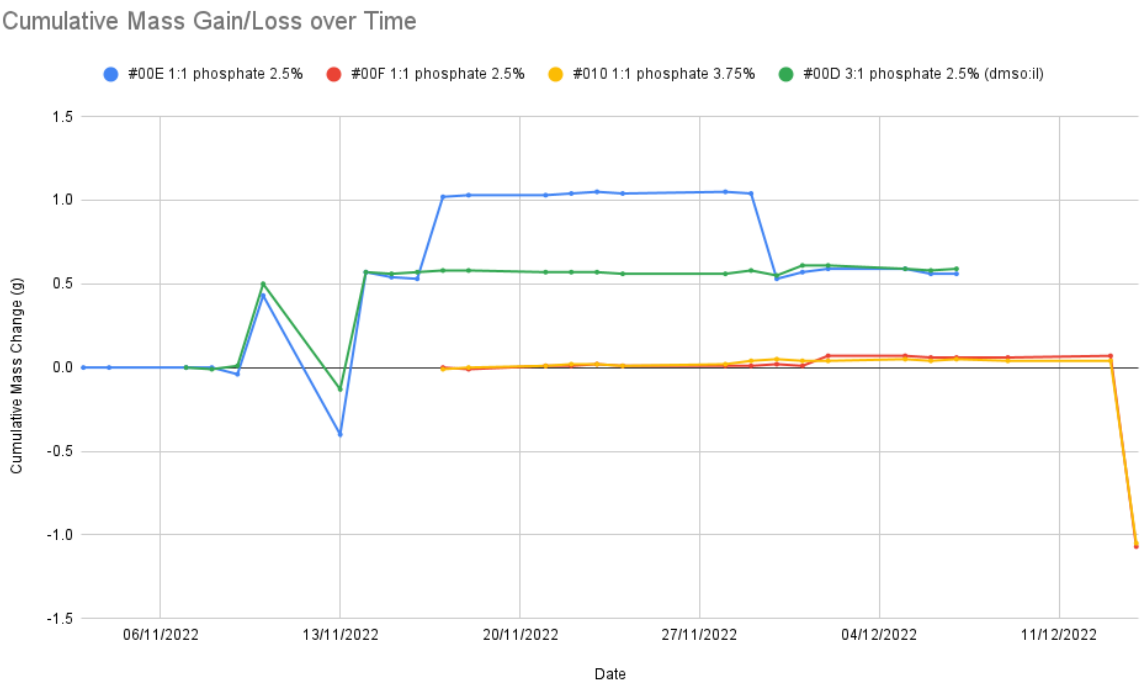
Electrospin a series of solutions as close to daily as possible, recording mass difference *between* the spins when idle.

The solutions spun where as follows:

- 1:1 Dimethyl sulfoxide to 1-Ethyl-3-methylimidazolium diethyl phosphate 2.5% Cellulose
- 1:1 Dimethyl sulfoxide to 1-Ethyl-3-methylimidazolium diethyl phosphate 2.5% Cellulose
- 1:1 Dimethyl sulfoxide to 1-Ethyl-3-methylimidazolium diethyl phosphate 3.75% Cellulose
- 3:1 Dimethyl sulfoxide to 1-Ethyl-3-methylimidazolium diethyl phosphate 2.5% Cellulose

The solutions were stored in the NanoQuEST cupboard in the corner of the lab, and as such were in an environment with variable humidity and temperature.

## Results




The graph above shows the cumulative mass gain/loss over time, that is, the sum of mass differences between spins, separated into distinct series for each solution. The #00D etc. refers to an internal stock ID number.

Our two 1:1 2.5% phosphate solutions were manufactured at the same time, and spun in parallel. There is a fluctuation between 10/11/23 and 13/11/23 that seems to self correct. This could be systematic error, as the two solutions behave in parallel.

A single 1:1 2.5% phosphate solution (#00E pictured in blue) suddenly gains 0.51g between 16/11/23 and 17/11/23, while no other solution does. It later loses a similar amount of mass, 'self correcting', between 29/11/23 and 30/11/23.

The 1:1 3.75% phosphate and 3:1 2.5% phosphate solutions behave in parallel quite reliable, and slowly gain mass, with a major anomaly between 13/12/23 and 314/12/23 where they suddenly losing a lot of mass. as they act in parallel with each other, it is lightly this is systematic error.

Overall all solutions seem to gain some mass, but with a lot of chaos.

The average mass change is +0.6g per 1.7 days.

## Comments and Uncertainty

Our mass uncertainty for individual measurements is +/- 0.2g, however there are factors that could raise this between measurements.

- We changed the mass scale we were using to measure midway though the experiment
- There might have been moisture or debris on the syringe / needle cap
- The scale may not have been tared to be set to zero before a measurement on any given day

The humidity and temperature the solutions were stored in was not tracked, and during the experiment there were some days with very high CO2 content and pollutants in the air that may have affected the humidity abnormally. (this was due to some soil burning in an adjacent lab).

The individual mass change measurements were often within the uncertainty range, makes it practically impossible to draw any significant conclusions from this data.

No solutions successfully formed nanofibers throughout the whole trial, which suggests significant issues with the solutions.

### Conclusions

We cannot draw any firm conclusions from this data. Due to the significant uncertainty in the data, we can neither accept or reject the null hypothesis.
However, ignoring outliers, there is a slight upwards trend in the cumulative mass difference. This does suggest that there is some change. We will investigate this further with a revised method.

## Method 2 (M2)

We are looking at how the age of solutions affects spin. M2 is testing if water gain could be responsible for the difference in ageing effects by storing solutions in a low humidity environment, and variable humidity environment.

All spinnable solutions within the ageing experiments are cellulose solutions, within M2 the only ionic liquid used was 1-Ethyl-3-methylimidazolium diethyl phosphate, as we do not currently have any 1-Ethyl-3-methylimidazolium acetate (which generally spins more reliably).

M2 also stores some non cellulose solutions as a control.

All ratios refer to Dimethyl sulfoxide : Ionic Liquid in that order without exception for this experiment.

If our hypothesis is correct, we expect to see some overall mass gain, as the cellulose is hydrophilic and will absorb water vapour when humidity is high.

## Methodology

Manufacture several different solutions, and split each one into two roughly equal beakers. Store one half in a tray in open air, and the other half in a desiccator.

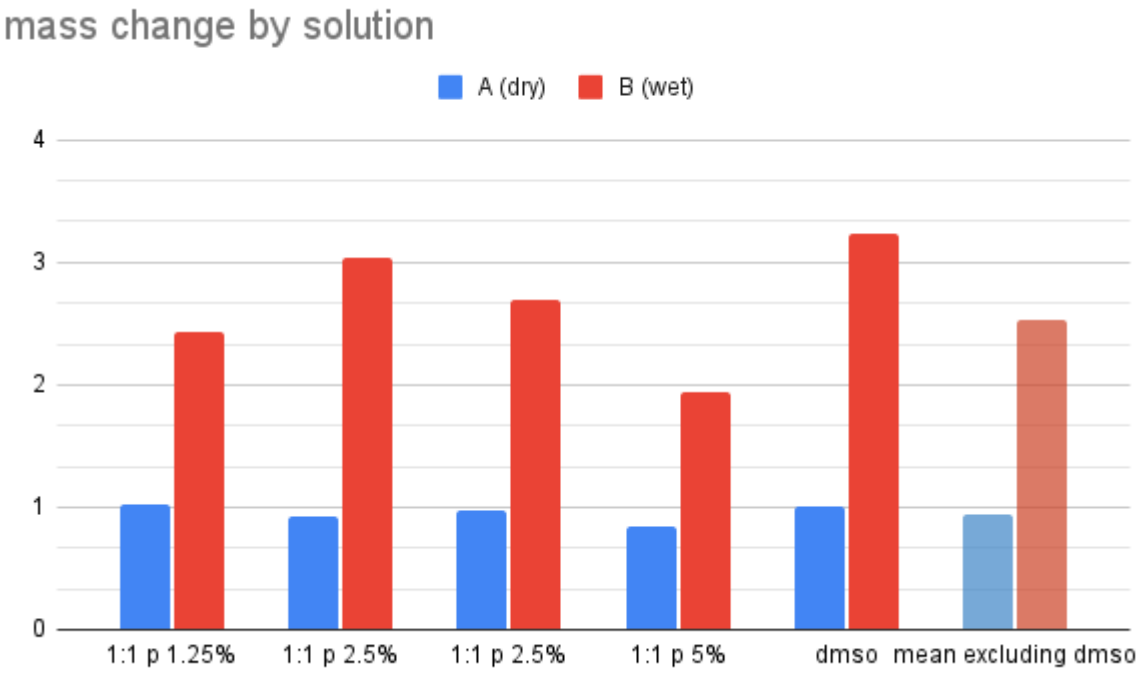
The solutions used are as follows:

- 1:1 Dimethyl sulfoxide to 1-Ethyl-3-methylimidazolium diethyl phosphate 1.25% Cellulose
- 1:1 Dimethyl sulfoxide to 1-Ethyl-3-methylimidazolium diethyl phosphate 2.5% Cellulose
- 1:1 Dimethyl sulfoxide to 1-Ethyl-3-methylimidazolium diethyl phosphate 2.5% Cellulose
- 1:1 Dimethyl sulfoxide to 1-Ethyl-3-methylimidazolium diethyl phosphate 5% Cellulose
- Dimethyl sulfoxide
- 4% 4M Polyethylene Oxide in distilled water

The humidity of the open air (wet) solutions were recorded by a data logger half hourly.

We expect the cellulose solutions to gain significantly more mass in wet storage than dry storage. If the DMSO is responsible for the take up in water, then it should also gain mass significantly more in wet storage in line with the cellulose solutions.

## Results




Our results show a significant mass gain in all cellulose solutions stored in variable conditions. The solutions stored in a low humidity environment, i.e. in the desiccator, gained significantly less mass by at least a factor of a half.
The solution that was only DMSO gained the most mass.

The average conditions of the wet solutions were 54% humidity at 15.9 C.
The solutions were left from 08/02/23 to 21/02/23.

## Conclusion and Comments

Our mass uncertainty per measurement was +/- 0.01g. Our mass gains are significantly higher than our uncertainties. Our results suggest that the solutions do in fact gain water vapour and this affects the solutions over time. The increase in mass outside the desiccator in the DMSO sample suggests that this gain is from the DMSO taking up water vapour, not the cellulose. This would make sense as there is far more DMSO than cellulose in any solution.

Increased water content will affect the conductivity and viscosity of solutions. We also observed that it caused the wet solutions to separate. This would happen much more slowly usually, as when they are stored in the needle they are in contact with the air far less.

Overall M2 has been far more reliable than M1 in results, and clearly indicates that the solutions do take up water vapour from the air.

# *Fun Random Other Stuff*

## ELECTROSPINNING NYLON

Nylon-6,10 is formed in a reaction between Hexane-1,6 diamine and decanedioyl chloride, forming a film of nylon where they meet.

### “””Nylon-6,10

Nylon-6,10 is made from two monomers, one contains six carbon atoms, the other 10 - hence its name. The 10-carbon monomer is decanedioyl dichloride (ClOC(CH2)8 COCl), an acid chloride with a -COCl group at each end. The other monomer is a six-carbon chain with an amino group, -NH2, at each end. This is 1,6-diaminohexane (H2 N(CH2)6 NH2, also known as hexane-1,6-diamine).

When these two compounds polymerise, the amine and acid groups combine, each time with the loss of a molecule of hydrogen chloride:

*n* ClOC-(CH2)8-COCl + *n* H2N-(CH2)6-NH2 → -(CO-(CH2)8-CONH-(CH2)6-NH)*n* - + *n* HCl

This polymer-forming process involving the loss of a small molecule is known as condensation polymerisation. “””[1]

See https://edu.rsc.org/download?ac=12243 (from footnote) for a common experimental method without electrospinning

**Method plan**

- both chemicals connects to a coaxial spinneret
- electrospin as normal, but with further safety considerations
- wash fibres in ethanol

Potential Problems

- Nylon forming too fast and clogging up the end of the needle
- safety (the chemicals want to kill us)

[1] Baker, C. (2006, February 28). *Making nylon | Exhibition chemistry*. RSC Education. Retrieved July 10, 2022, from https://edu.rsc.org/exhibition-chemistry/making-nylon/2020063.article