Wettability of aqueous LiTFSI on graphite using Molecular Dynamics

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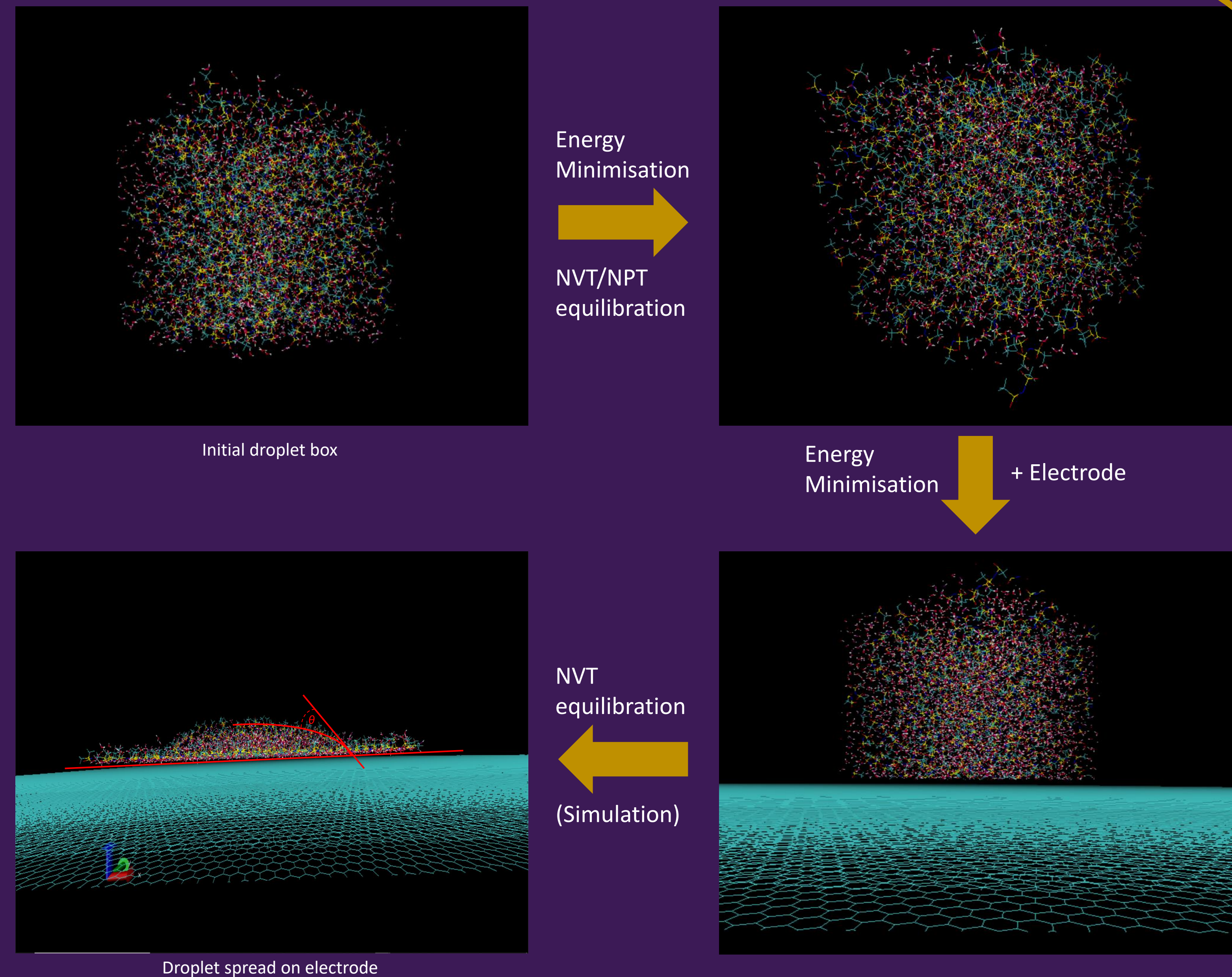
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AIMS + OBJECTIVES -

- Wetting is a measure of how well the droplet covers the surface, typically quantified by contact angle measured in degrees (°).
- A lower contact angle represents a better spread across the surface and therefore increased interaction between the liquid and solid mediums.
- This dissertation investigates the effects of concentration and temperature on contact angle.

BACKGROUND + CONTEXT -

- Water-in-salt electrolytes are popular alternatives to alkaline solutions such as $LiPF_6$ in energy storage systems.
- They are cheaper, safer, and more environmentally friendly[1].
- WIS electrolytes by definition have more salt than water by mass (for LiTFSI this is ~5m).
- LiTFSI improves the Electrostatic Stability Window from 1.23V in pure water to 3V at 21m concentration due to formation of a protective layer at the anode (solid electrolyte interphase)[2].
- As concentration increases, density and viscosity increase[3].
- This leads to a decrease in diffusion coefficients so the system evolves more slowly.
- Concentration increases the ion transport number[3].
- Maximum ionic conductivity at ~5m which decreases as concentration increases[4] but increases with temperature.
- TFSI$^-$ is an amphiphile meaning it exhibits both hydrophilic and hydrophobic behaviour.

Initial droplet box

Energy Minimisation

NVT/NPT equilibration

Energy Minimisation + Electrode

NVT equilibration (Simulation)

Droplet spread on electrode

METHOD –

- During simulation, certain values must be conserved – the most important being the total energy of the system.
- The behaviour of atoms is described by the equations of motion which are functions of momentum and charge.
- The system evolves in both the spatial (translation and rotation) and temporal domains using 'kick' and 'drift' methods.
- Energy minimisation ensures an appropriate starting configuration for the droplet
- Temperature and pressure are set during NVT/NPT equilibration respectively, using thermostats and barostats.
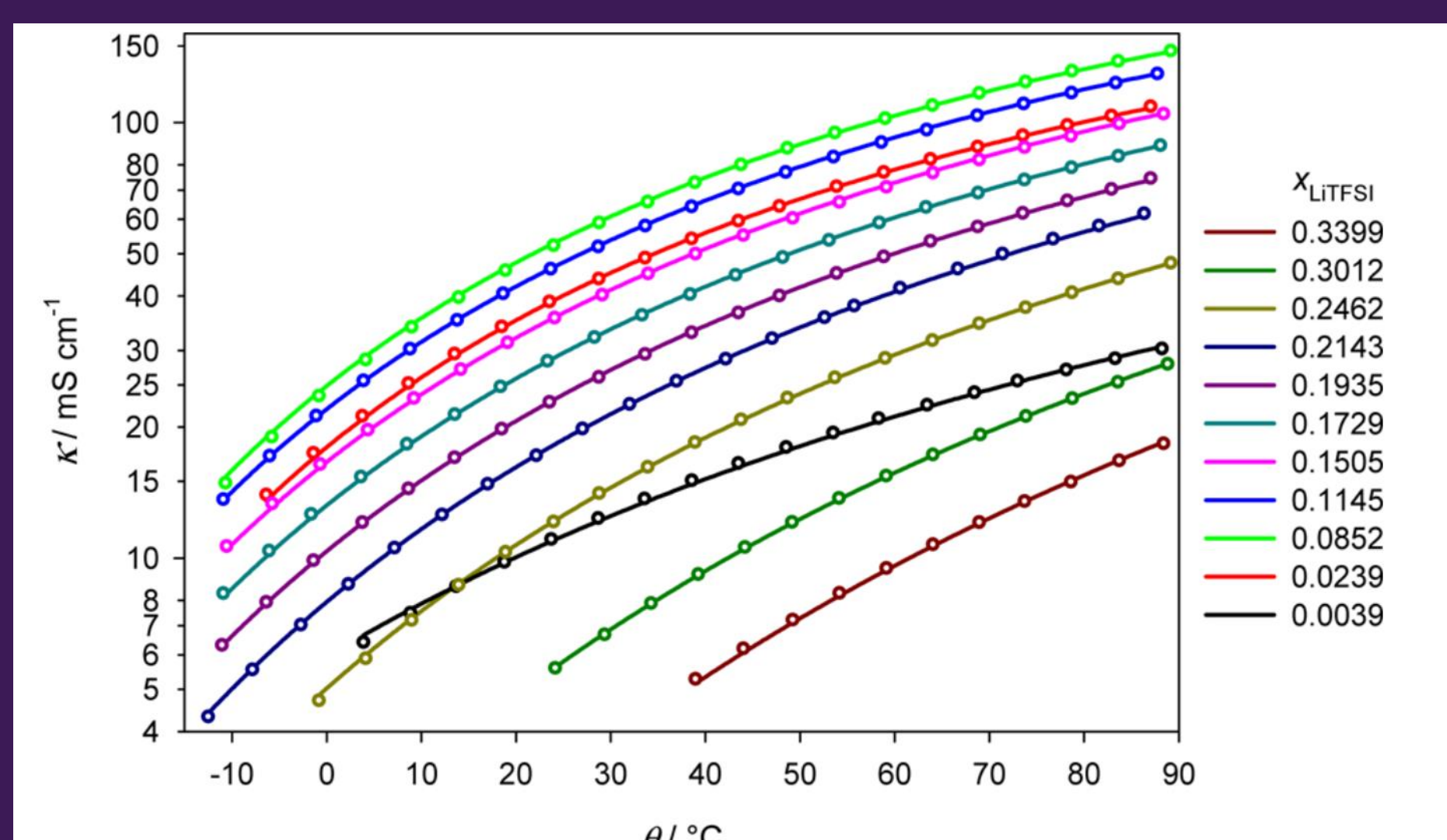
Graph showing the change in ionic conductivity with temperature for different concentrations[4]

x_{LiTFSI}
- 0.3399
- 0.3012
- 0.2462
- 0.2143
- 0.1935
- 0.1729
- 0.1505
- 0.1145
- 0.0852
- 0.0239
- 0.0039

$$\cos(\theta) = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$ Young's Equation

- The contact angle can be represented as a function of the 3 different interfacial tensions between the solid, liquid, and vapour components.
- These tensions are governed by the cohesive (within droplet) and adhesive forces (i.e. between solid and liquid) of the system.
- Wetting is influenced by factors such as concentration, temperature, pressure, and applying a potential difference across the electrode.

Concentration vs Contact Angle
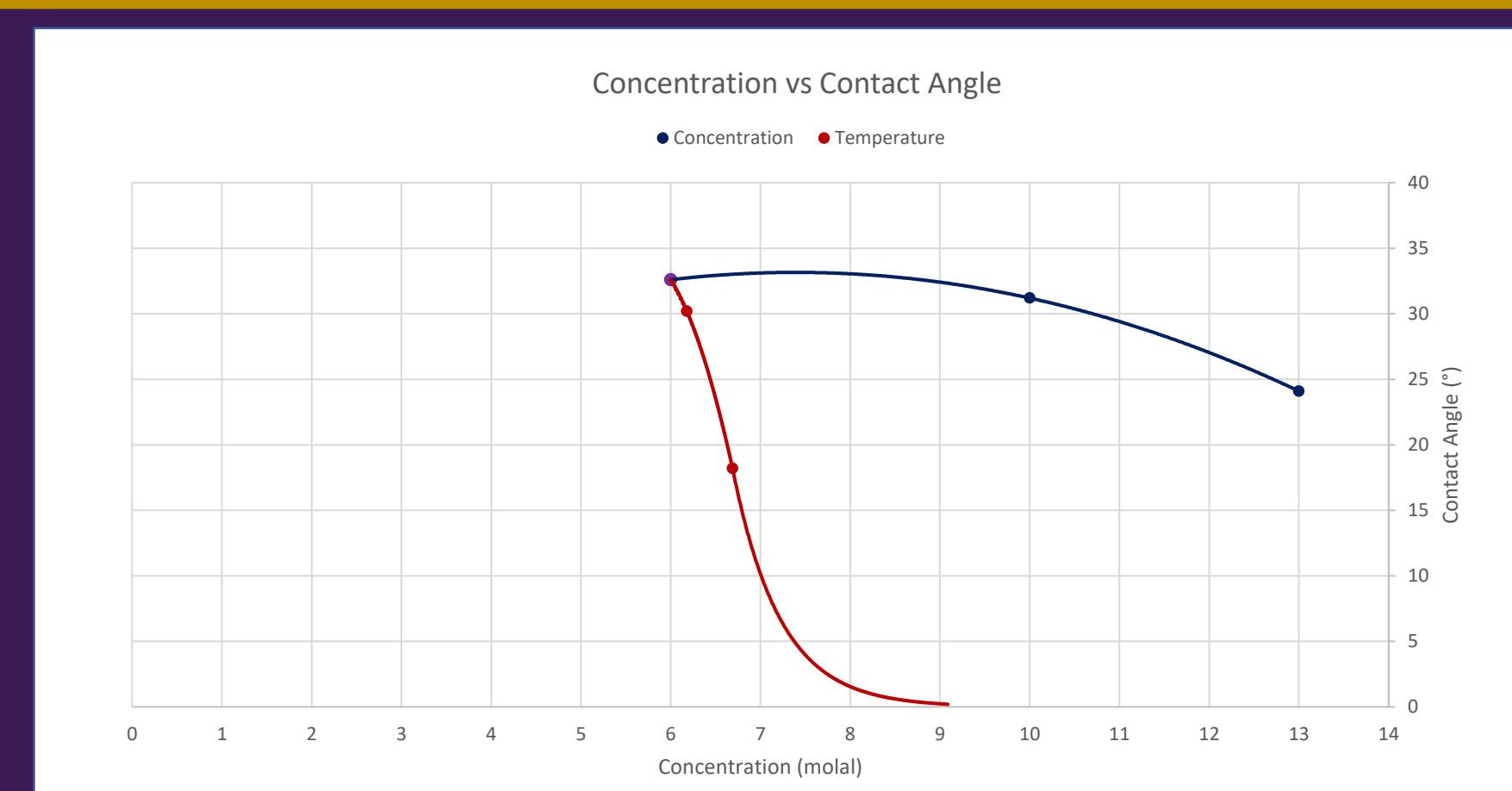
RESULTS -

- Increasing concentration decreases the contact angle shown by the blue line on the graph to the right (25°C).
- TFSI$^-$ break the H-bonds between water molecules and forms electrostatic forces of attraction with them.
- The anions are preferentially absorbed to the droplet surface and electrode surface which decreases γ_{LV} and γ_{SL}.
- Applying a p.d. across electrodes will increase or decrease the contact angle for LiTFSI (aq) depending on the magnitude and pole of the surface[5].

- Increasing temperature improves contact angle significantly as shown by the red line on the graph above (represented as equivalent concentrations: at 25°C, 50°C, 75°C, 100°C).
- Water is preferentially evaporated, increasing concentration of the droplet.
- The addition of steam into the system will also impact γ_{LV} and γ_{SV}.
- The cohesive forces within the liquid are weakened as energy is added to the system, thus encouraging better spreading of the droplet.

References:

[1] - Li, W., Dahn, J.R. and Wainwright, D.S. (1994) 'Rechargeable lithium batteries with aqueous electrolytes', *Science*, 264(5162), pp. 1115–1118. doi:10.1126/science.264.5162.1115.

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[3] - Zhang, Y. and Maginn, E.J. (2021) 'Water-in-salt litfsi aqueous electrolytes (2): Transport properties and li+ dynamics based on molecular dynamics simulations', *The Journal of Physical Chemistry B*, 125(48), pp. 13246–13254. doi:10.1021/acs.jpcb.1c07581.

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[5] - Papaderakis, A.A. *et al.* (2023) 'Dielectric-free electrowetting on graphene', *Faraday Discussions*, 246, pp. 307–321. doi:10.1039/d3fd00037k.