

Insights into Aqueous Glyoxal Chemistry via Glass Transition Measurements

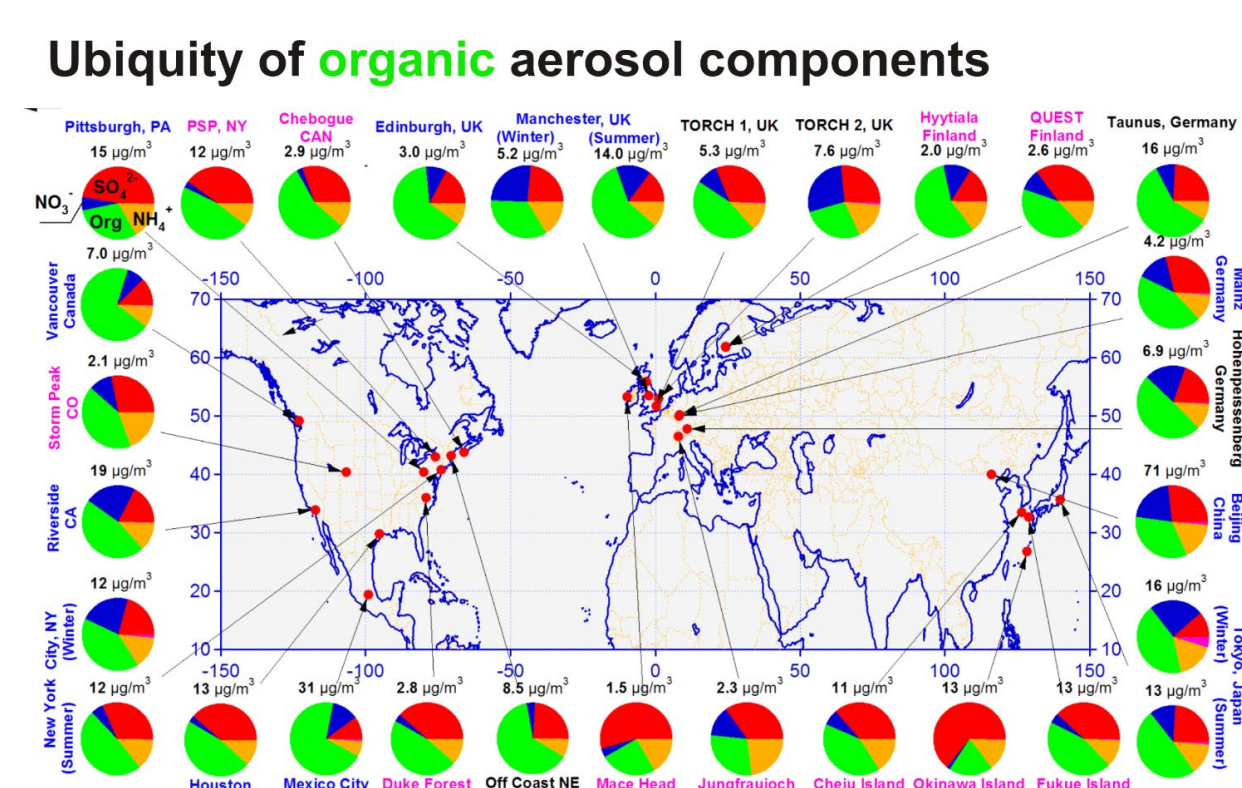
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Introduction

Aerosols greatly influence various processes in Earth's atmosphere through different direct and indirect effects. The extent of this influence, however, is not well understood, in part because aerosol properties such as the phase state are often variable and uncertain.

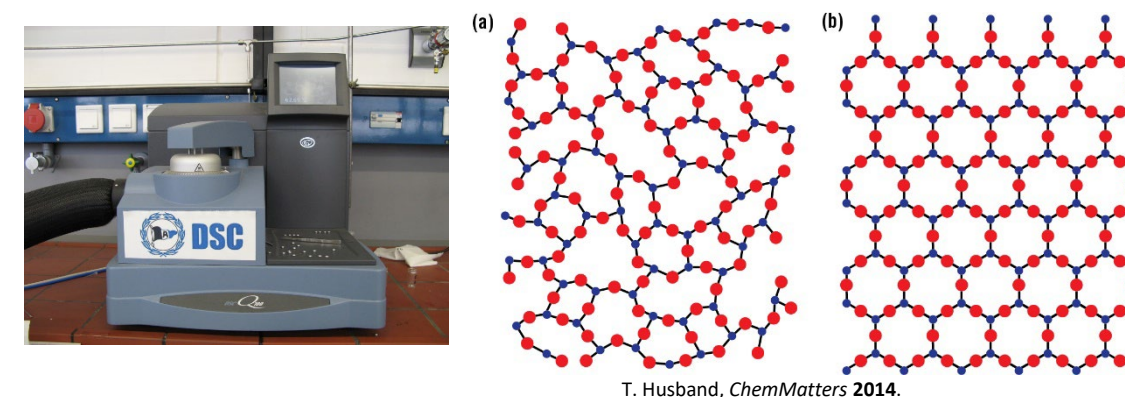
In contrast to most inorganic species, which are known to form crystalline aerosol particles, aerosols consisting of organic compounds and their mixtures with other organic and/or inorganic species may form liquid or glassy particles.^[1]



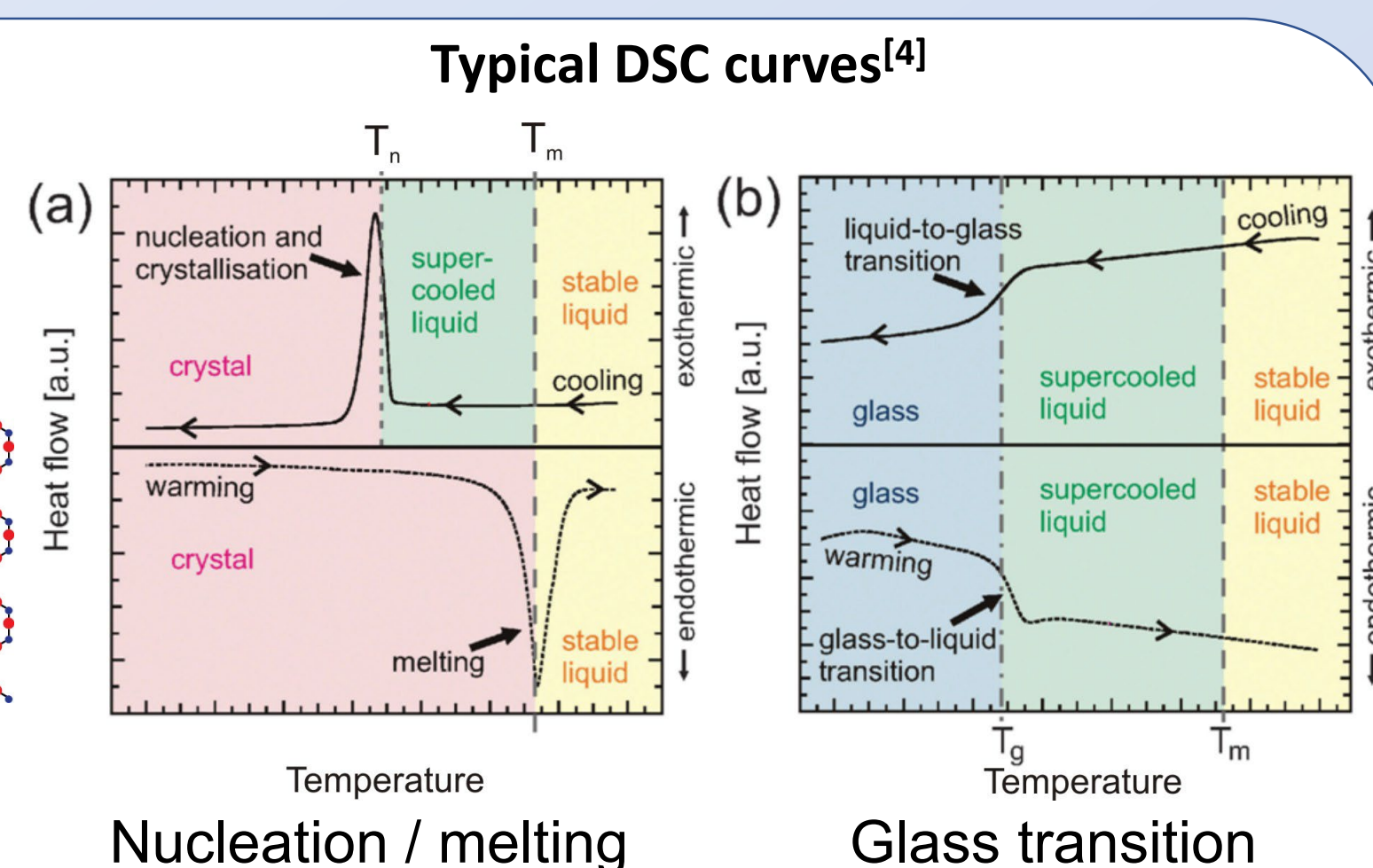
Rising question:
 Phase state of mixed aerosol particles:
 Are they crystalline, liquid or glassy?

DSC & Glass

Differential Scanning Calorimetry

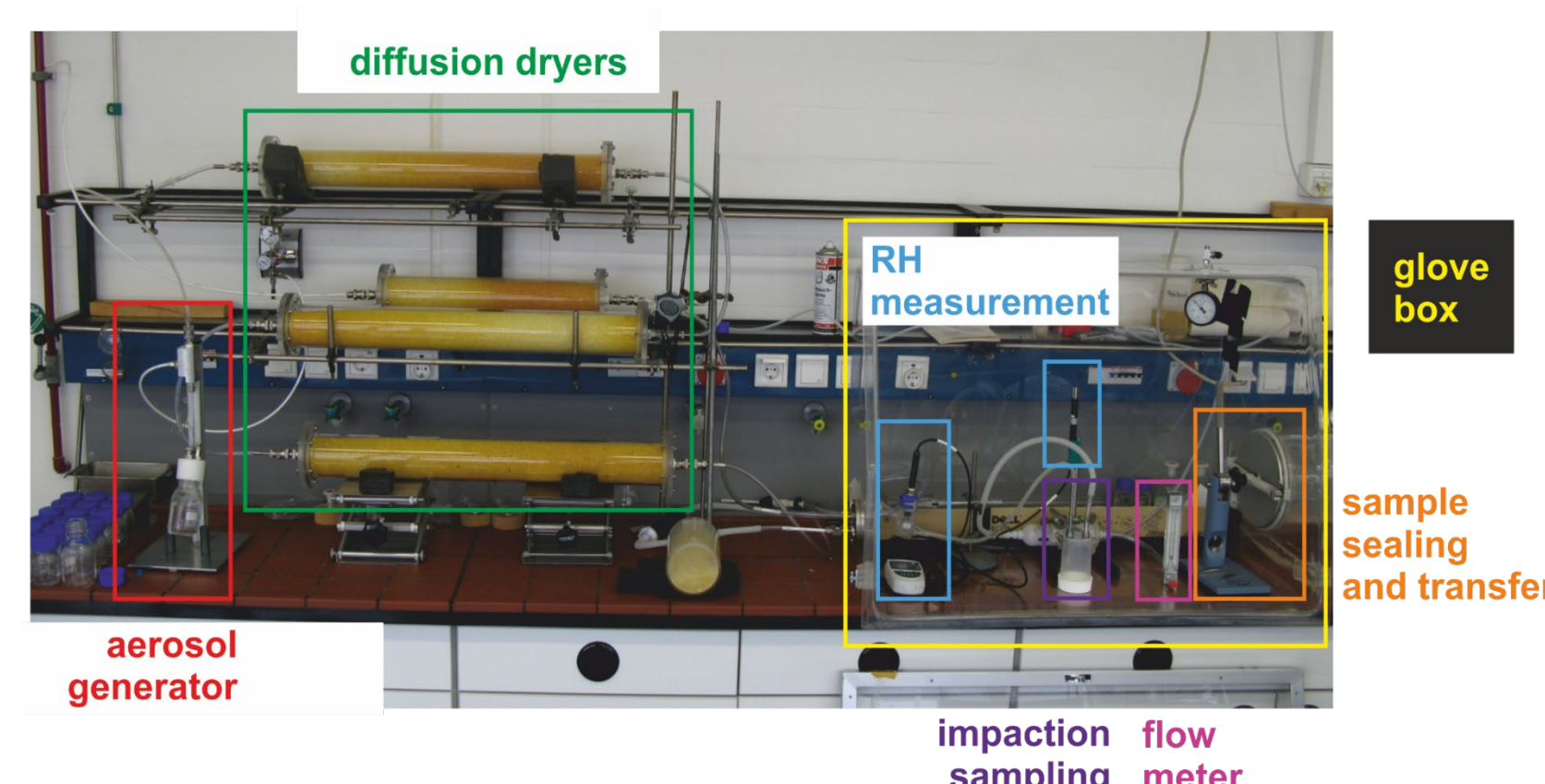
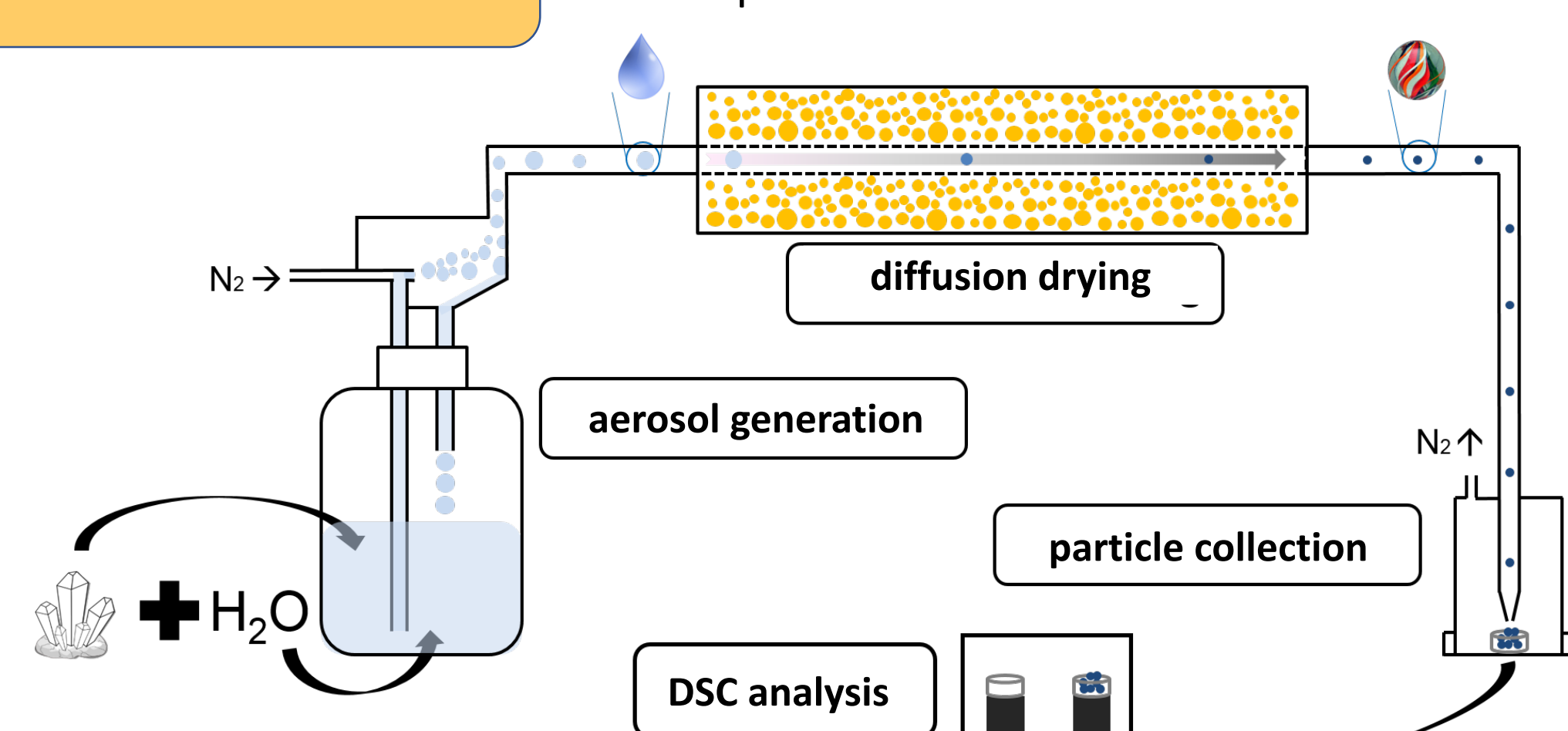


Glass: Non-crystalline amorphous solid without long-range molecular order but mechanical properties of a solid.^[4]



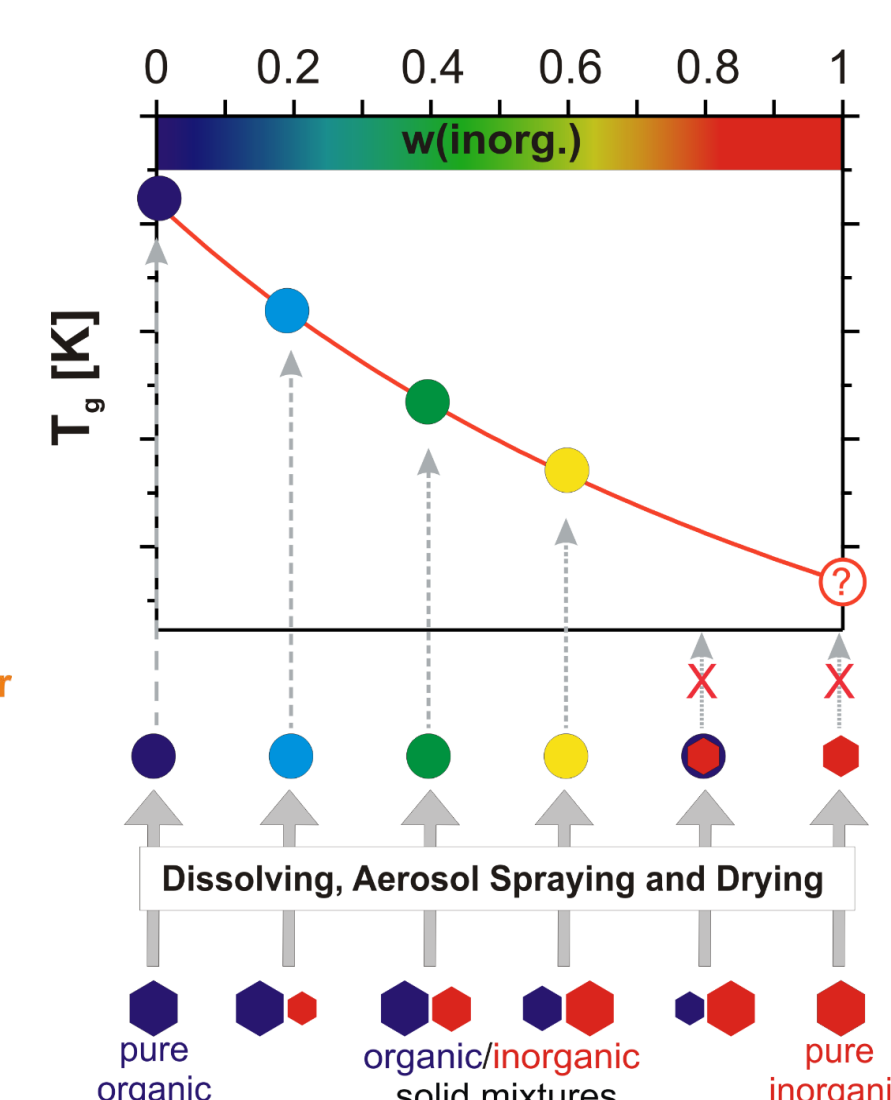
MARBLES*

*Metastable AeRosol By Low temperature Evaporation of Solvent^[2,3]



Advantages:

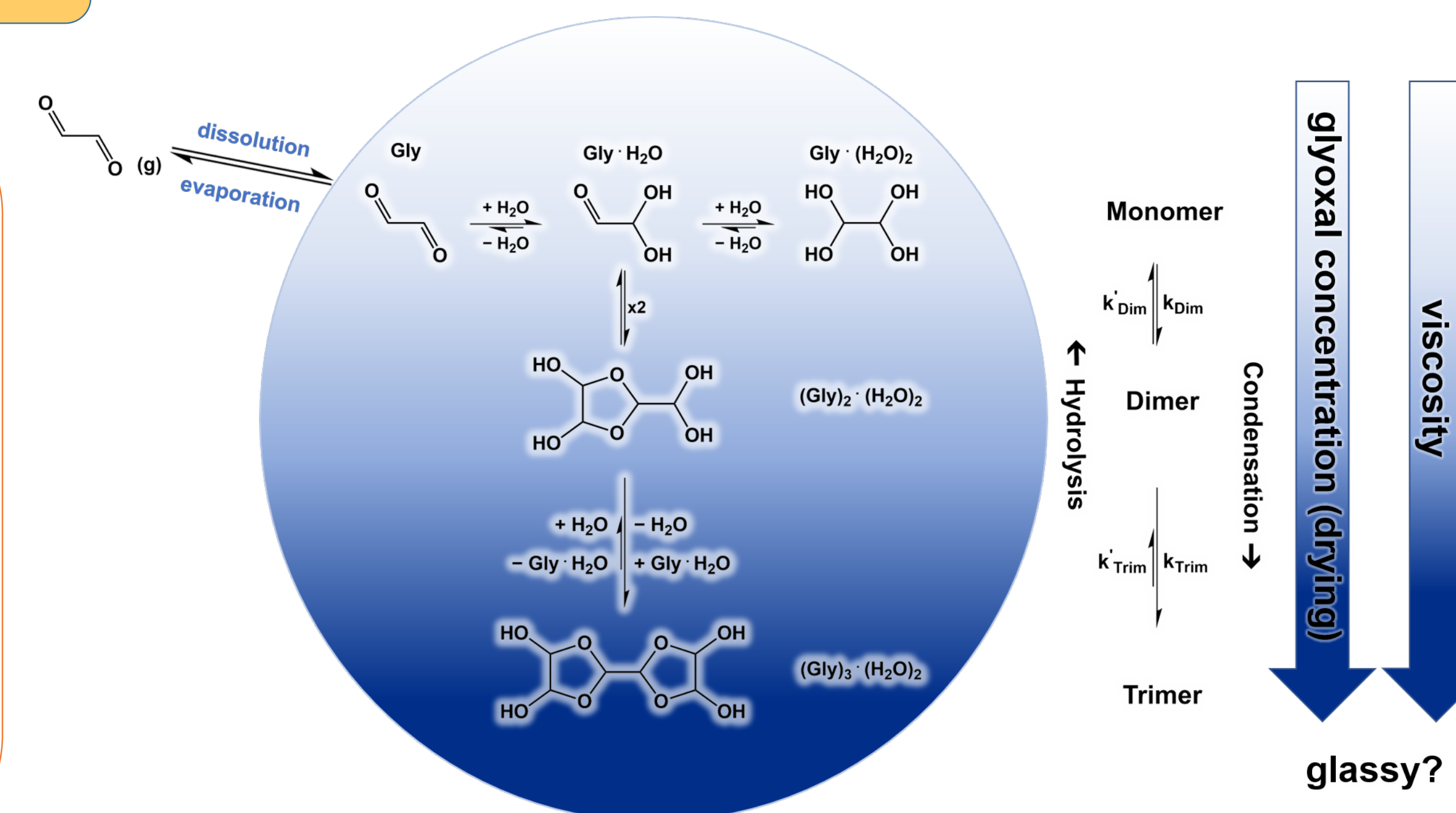
- Glass formation at room temperature
- Small probability of crystallization because of small individual airborne droplets
- Fast glass formation on the timescale of seconds
- No further sample preparation needed
- Study of multicomponent mixtures possible



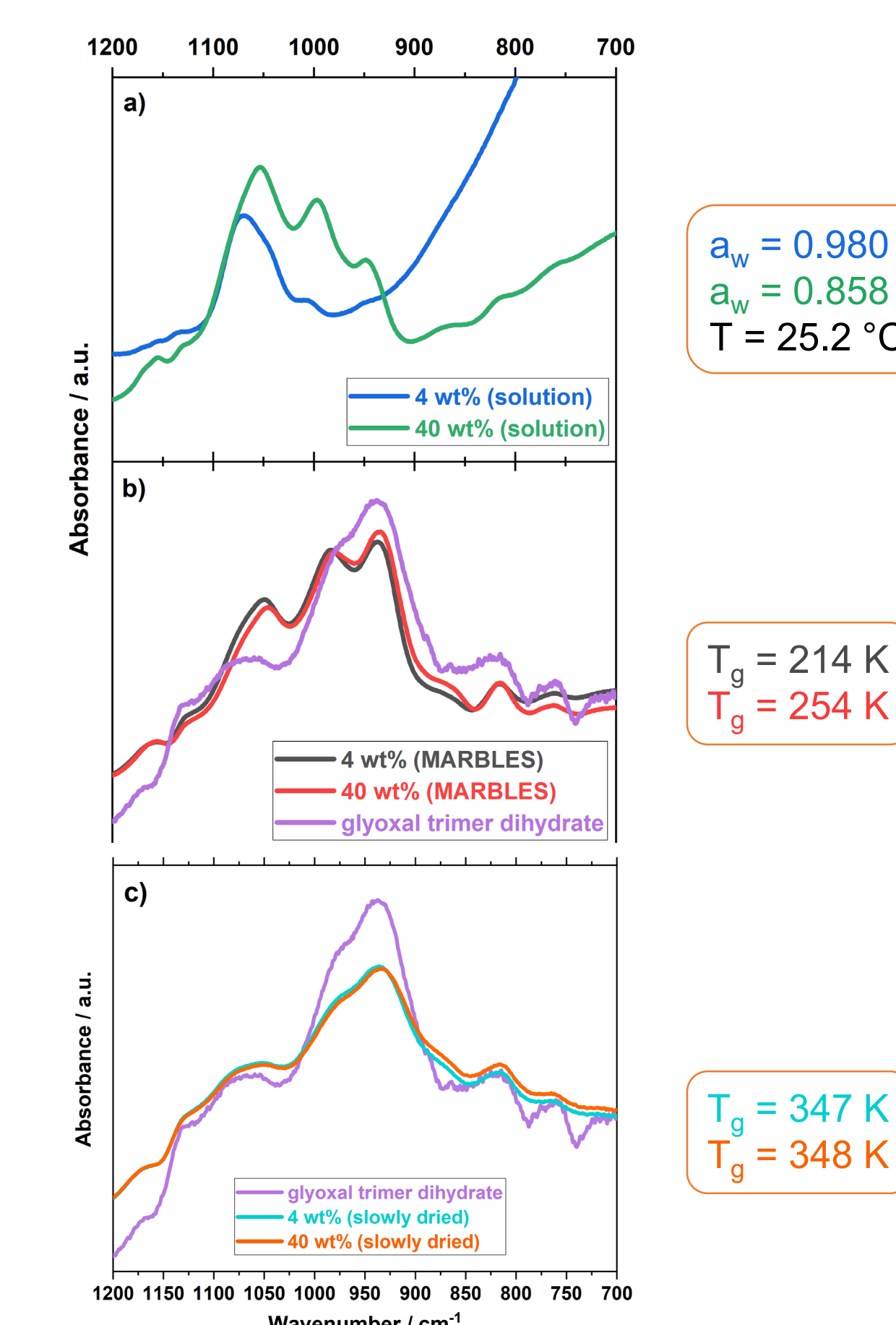
Amorphous Glyoxal Particles

- Glyoxal is highly abundant in the troposphere (≈ 45 teragram per year^[5]) due to direct emission or formation of SOA
- Despite high vapour pressure, glyoxal contributes to the formation of aerosol particles (see aqueous glyoxal chemistry on the right)
- Glyoxal has a large Henry's law constant and readily forms dimeric and trimeric water adducts^[6]
- Chemical equilibria shift from monomeric and dimeric towards dimeric and trimeric glyoxal species for higher concentrations (e.g. during drying)
- No studies of glass transition temperatures in aqueous glyoxal systems have been reported

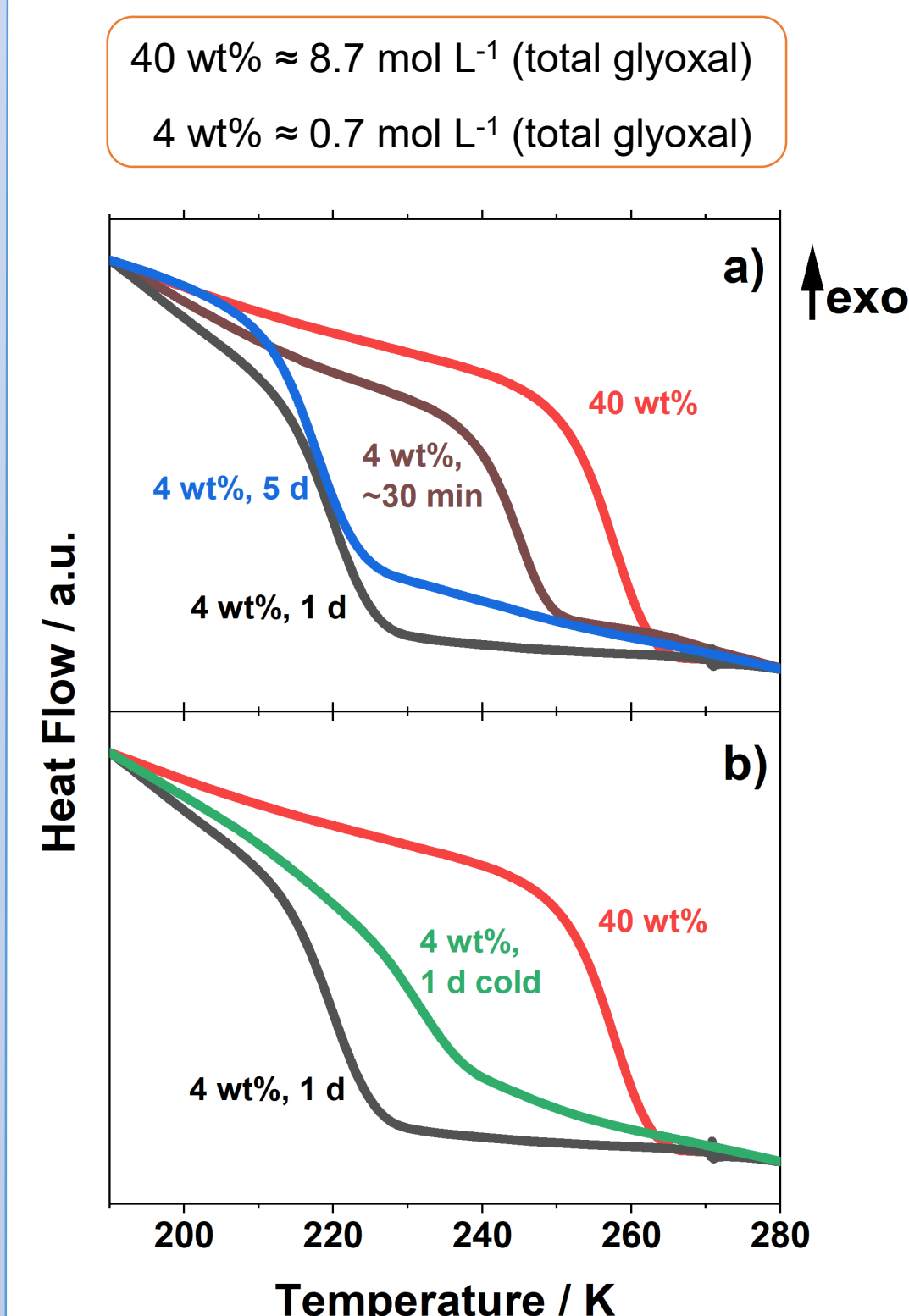
Aqueous Glyoxal Chemistry



ATR-IR Spectra



DSC Measurements of MARBLES Samples



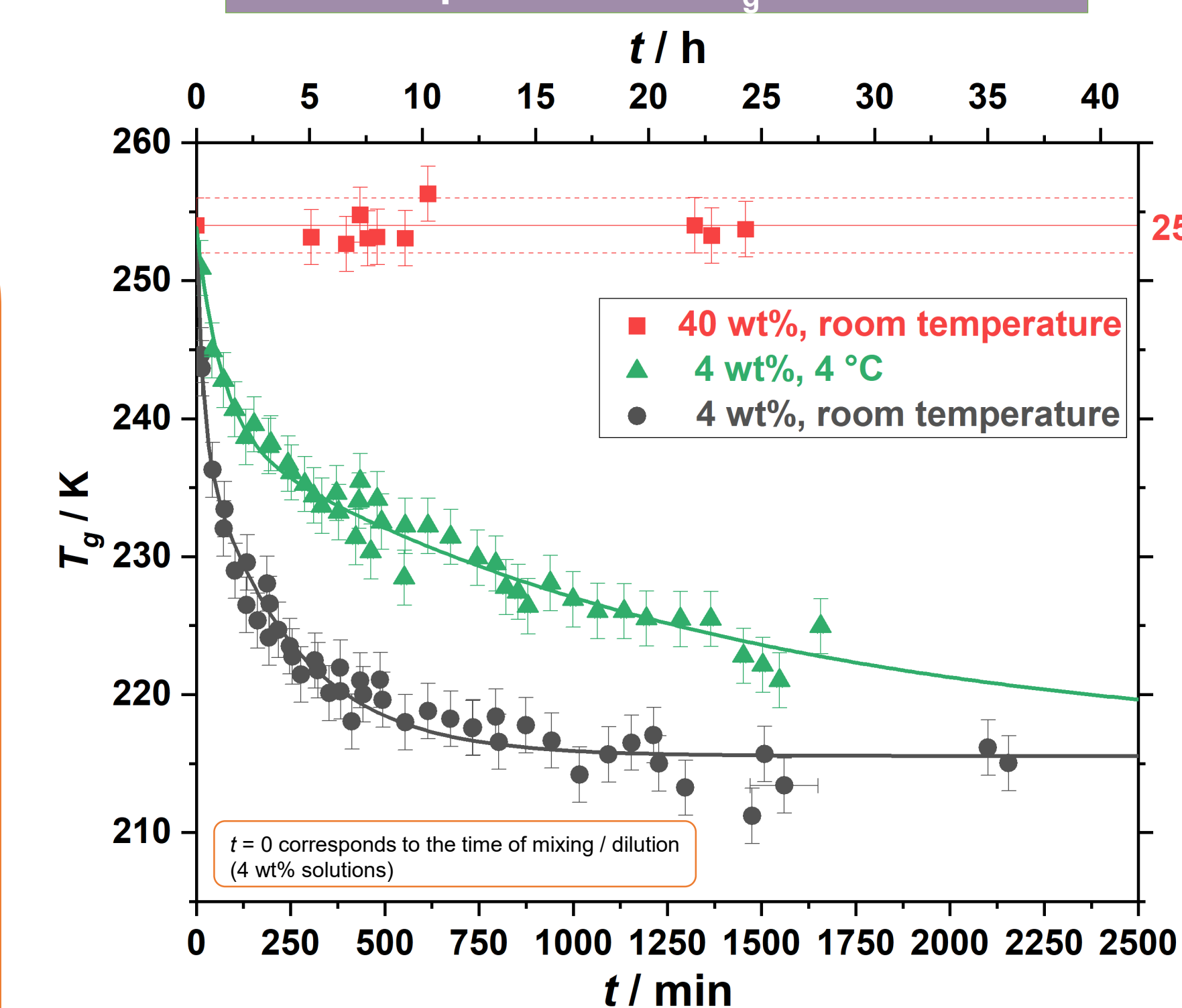
Further Reading

J.-H. Peters, H. P. Dette, T. Koop, *ACS Earth Space Chem.* **2021**, *5*, 3324.



- Left:** T_g of MARBLES-dried aqueous glyoxal solutions
- a) T_g of a dried 40 wt% solution (red) differs significantly from an equilibrated diluted 4 wt% solution at RT (blue). T_g also varies with time after dilution (brown)
- b) T_g of a dried solution that has been cooled since dilution (green) differs from a diluted solution stored at room temperature (black)
- The underlying chemical processes are temperature and time dependent
- Right:** Detailed investigation of the temperature and time dependence of T_g
- Repeated drying of a 40 wt% solution (red) shows no change (exclusion of influences due to the setup)
- T_g of a diluted solution decreases with time after dilution. The decline is stronger at room temperature (black) when compared to a solution at 4 °C (green)
- Two chemical processes dominate the chemistry in aqueous solution: trimer hydrolysis and dimer hydrolysis

Time Dependence of T_g after Dilution



$$T_g(t) = T_{g,t=0} + A_1 \cdot \exp\left(-\frac{t}{\tau_1}\right) + A_2 \cdot \exp\left(-\frac{t}{\tau_2}\right)$$

	T _{g,t=0} / K	A ₁ / K	τ ₁ / min	A ₂ / K	τ ₂ / min
room temp.	215.6 ± 0.4	14.4 ± 1.1	17 ± 4	23.3 ± 0.8	241 ± 18
4 °C	216.1 ± 0.8		65 ± 13		1319 ± 135



E_A(τ₁) ≈ 56 kJ mol⁻¹ E_A(τ₂) ≈ 71 kJ mol⁻¹
 Trimer hydrolysis Dimer hydrolysis^[7]

- Top:** ATR-IR spectra of equilibrated glyoxal solutions (a), fast dried equilibrated glyoxal solutions (b) and slowly dried glyoxal solutions in comparison with the glyoxal trimer dihydrate (c)
- a) Bands with maxima at lower wave numbers are visible due to the equilibrium shift towards trimeric glyoxal species for higher concentrated solutions (green)
- b) Fast dried equilibrated glyoxal solutions are quite similar (black and red) despite differing significantly in T_g
- c) In slowly dried equilibrated glyoxal solutions (turquoise and orange), the trimer (purple) is the dominant species

Conclusion

- Glyoxal forms highly viscous particles upon fast and slow drying
- Equilibration time after dilution, mimicking water uptake in the atmosphere, is slow – especially for low temperatures
- T_g measurements can be used to infer information on the aqueous chemistry of organic molecules in solution in slowly equilibrating systems

References

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