Discontinuous hygroscopic growth of a mixed organic/inorganic aerosol particle levitated in an electrodynamic balance

By

Vacharaporn Soonsin

Supervisors

Prof. Thomas Peter

Dr. Ulrich Krieger

Institute for Atmospheric and Climate Science

ETH Zurich, Switzerland

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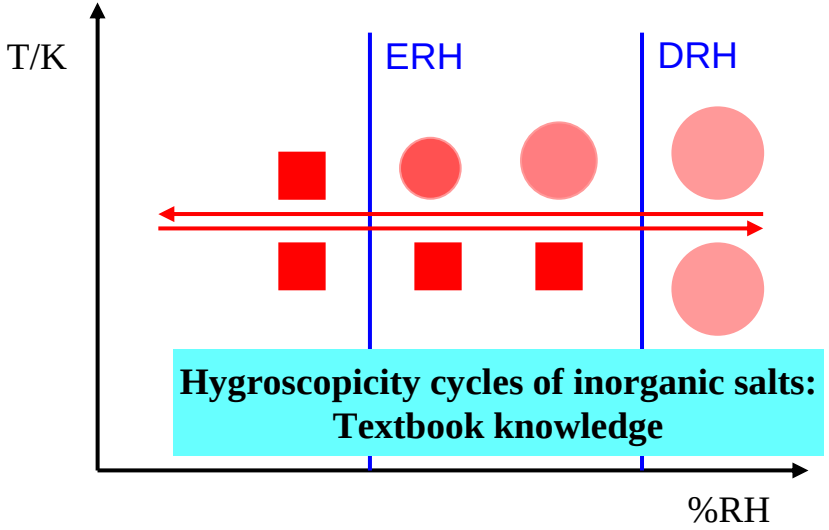
Outlines

- Introduction
- Experimental setup
- Preliminary experiments
- Conclusion
- Take home messages

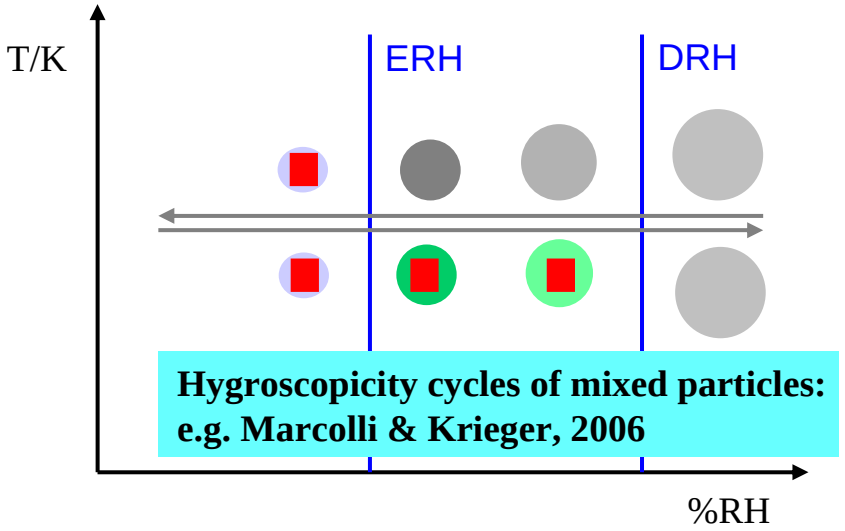
Phases and phase changes of aerosol particles

Inorganic salt e.g. NaCl, $(NH_4)_2SO_4$



Hygroscopicity cycles of inorganic salts: Textbook knowledge

Mixed organic/inorganic particles



Hygroscopicity cycles of mixed particles: e.g. Marcolli & Krieger, 2006

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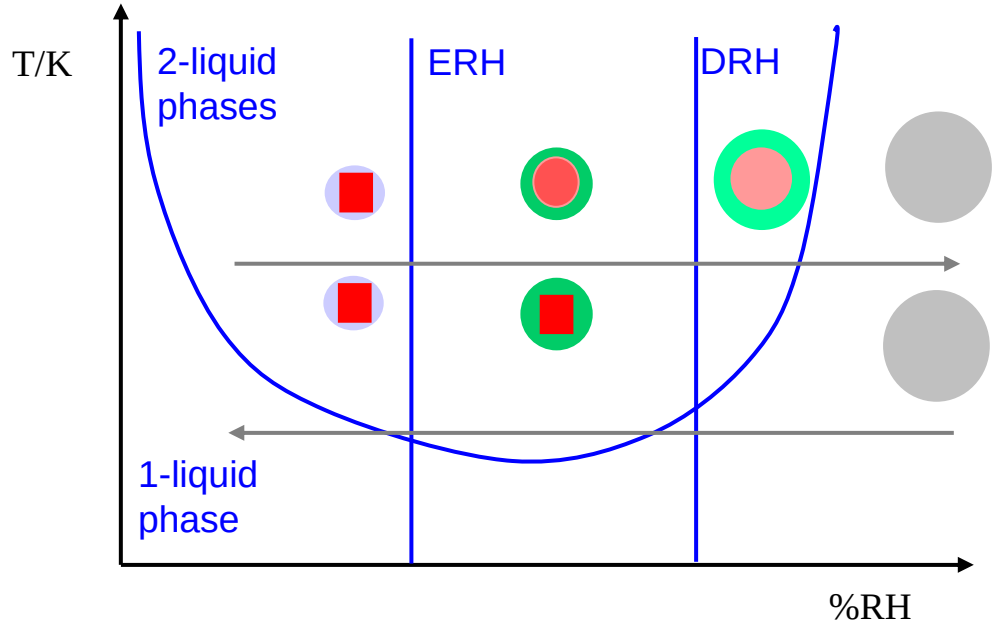
Phases and phase changes of aerosol particles

Mixed organic/inorganic particles with liquid-liquid phase separation



Influence of liquid-liquid phase separation on hygroscopicity cycles

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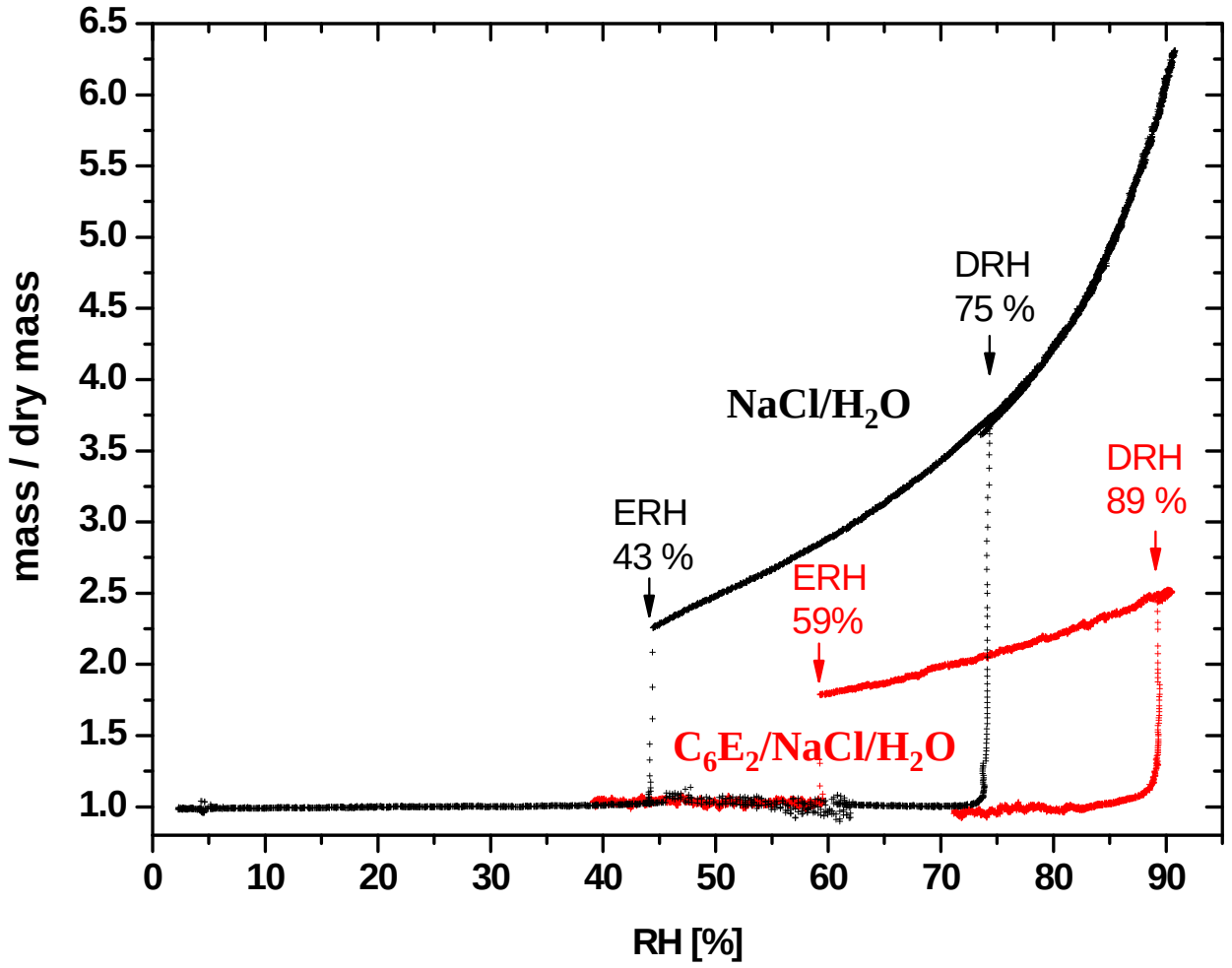
Hygroscopicity cycle from the EDB



C_6E_2
Diethylene glycol monohexly ether
$CH_3(CH_2)_5(OCH_2CH_2)_2OH$

C_6E_2/NaCl/H_2O with mole ratio of NaCl/C_6E_2 = 0.32
Particle dry size = 5 µm, Temp. = 288 K

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Chemical properties

Properties	C_6E_2 [Diethylene glycol monohexyl ether]	C_8E_4 [Tetraethylene glycol monooctyl ether]
Chemical formular	$C_{10}H_{22}O_3$ $CH_3(CH_2)_5(OCH_2CH_2)_2OH$	$C_{16}H_{34}O_5$ $CH_3(CH_2)_7(OCH_2CH_2)_4OH$
Molecular weight	190.28	306.44
Density [g/cm^3]	0.933	0.970
Enthalpy of vaporization [kJ/mol]	57.80	74.58
Polar surface area [Å^2]	38.7	57.2
Vapor pressure [Torr]	**1.82×10^{-3}**	**7.08×10^{-8}**

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Experimental setup

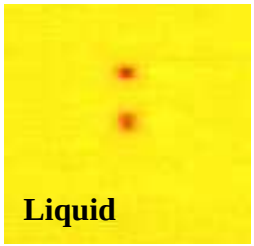
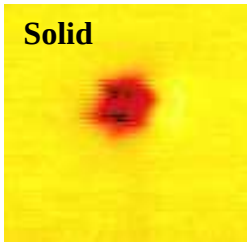
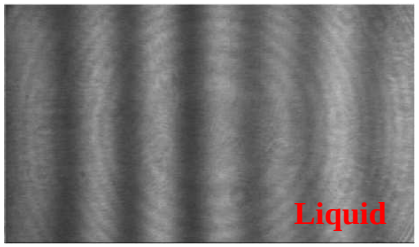
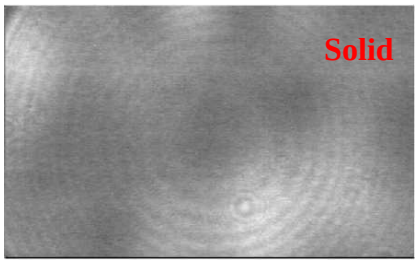


Image of particle

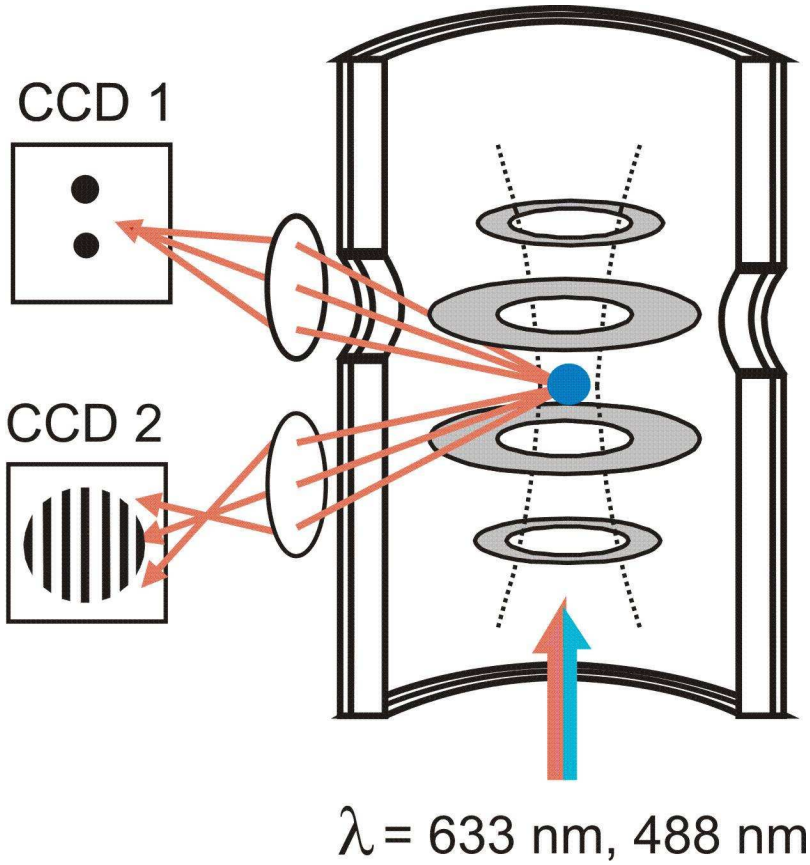




Scattering pattern of particle



Electrodynamic balance : EDB



Ref: Zardini et. al., Optical Express 2006

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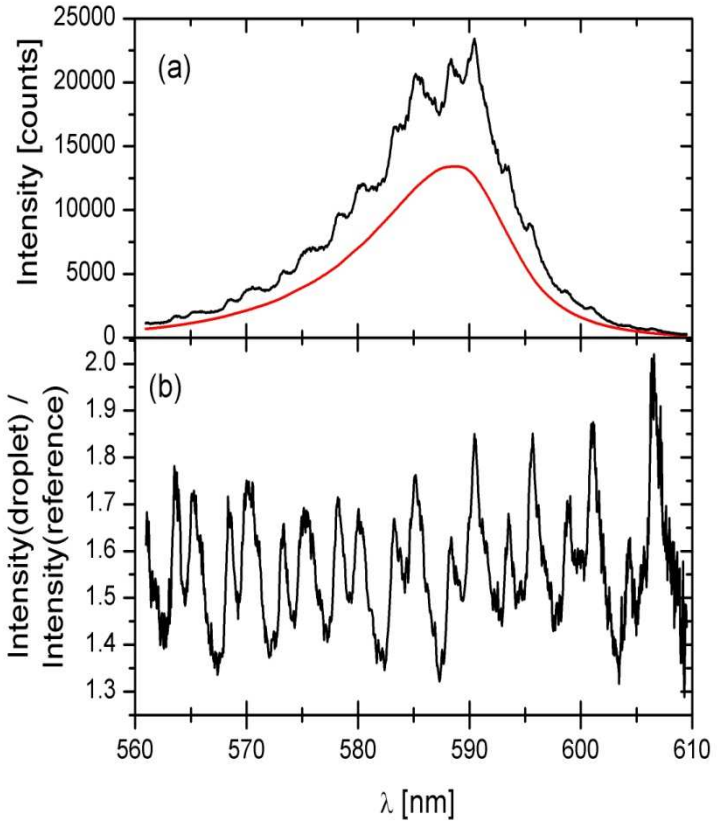
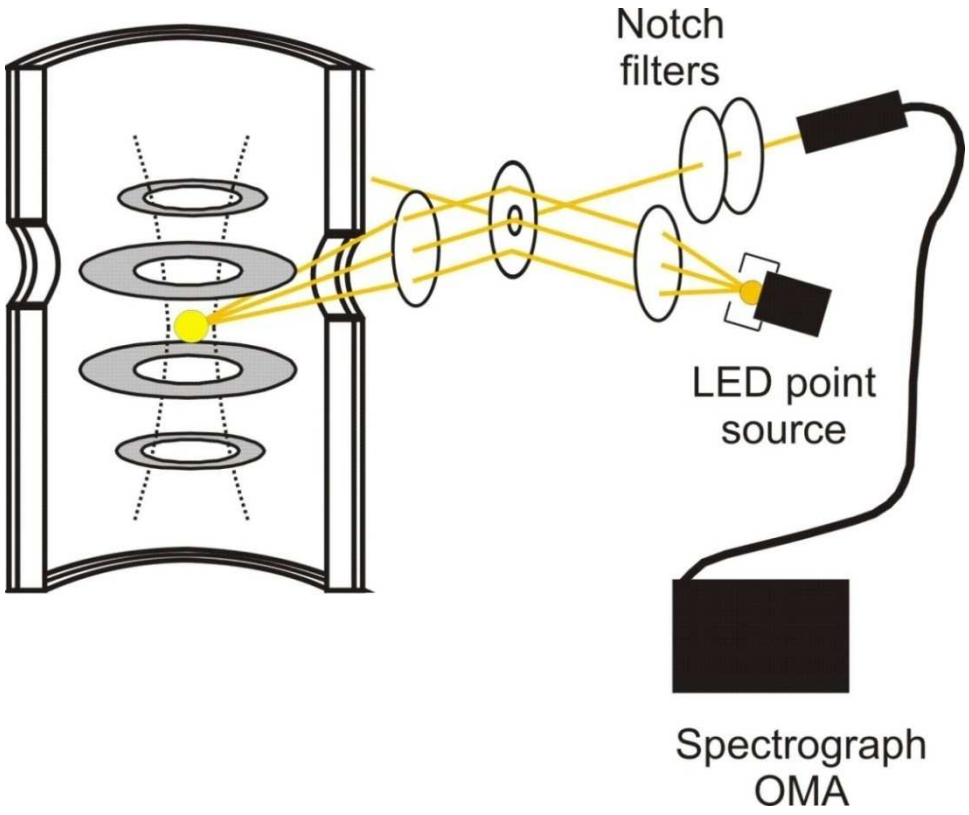
Experimental setup

Electrodynamic balance : EDB





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Methods to characterize aerosol particle

1. The DC voltage applied to compensate the gravitational force is proportional to and a measure for the mass of the particle.
2. Mie phase functions are used to deduce the radius of the particle and to detect phase changes.
3. Raman spectroscopy is employed to measure the particle's composition.
4. The radius of a liquid (spherical) particle can be measured with high precision using a tunable diode laser or a LED-"white"-light source [Zardini et al., 2006] and analyzing the Mie resonance spectra.
5. Temporal light-scattering fluctuations and spatial asymmetry in the 2D scattering patterns are used to deduce solid-to-liquid partitioning as well as phase changes and morphology of the aerosol particle.

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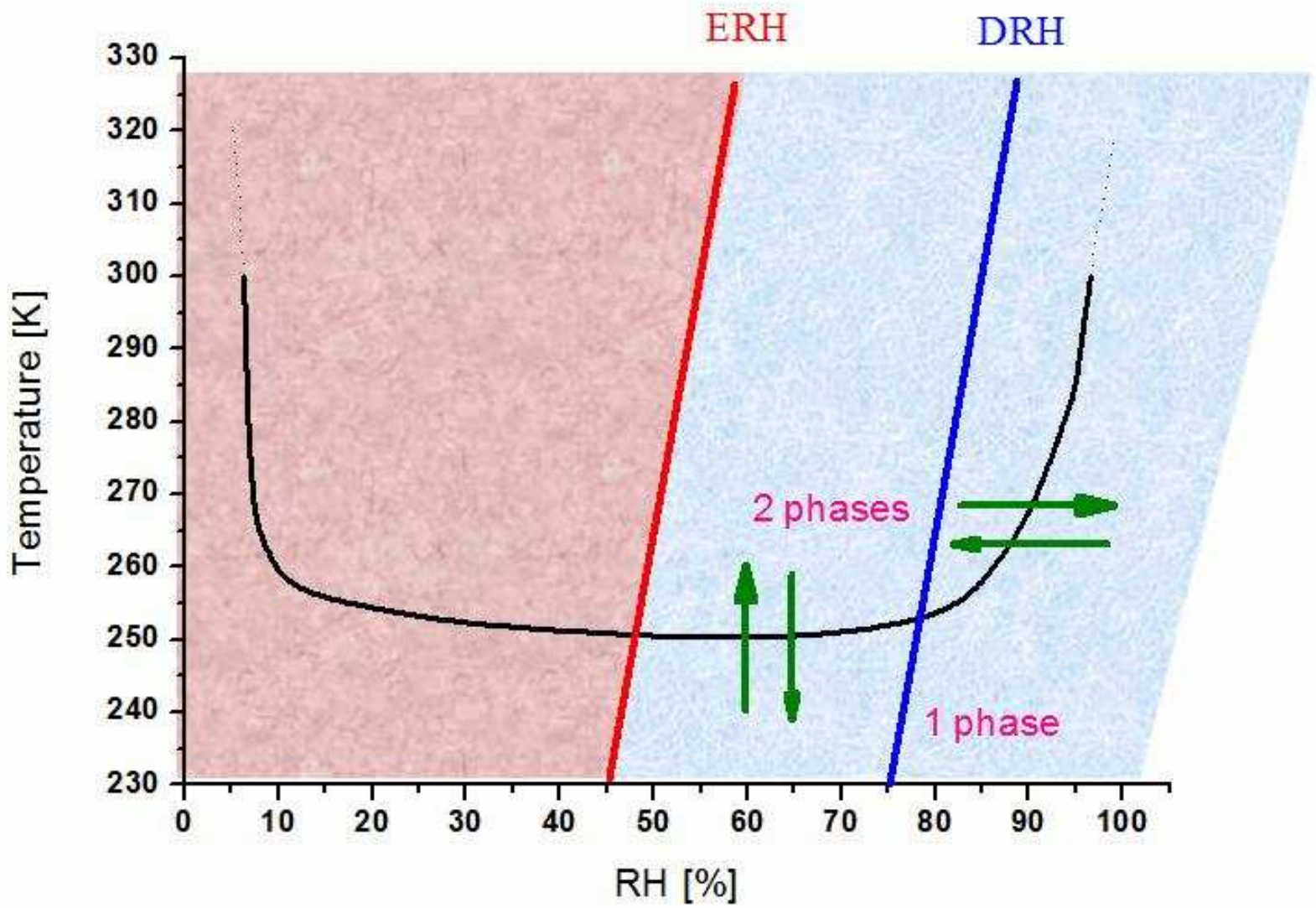
Different pathways through phase diagram



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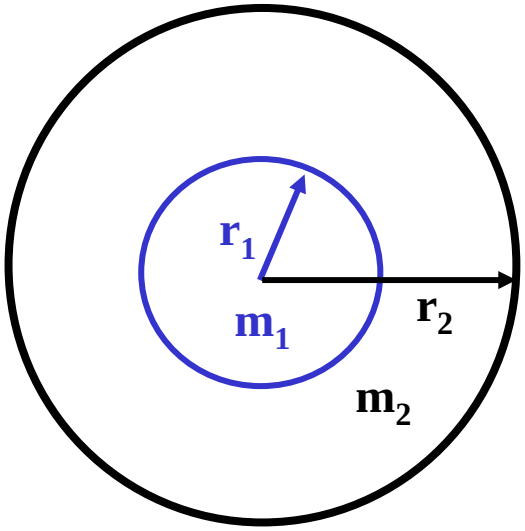
Mie Resonance Modeling



$$Mie\ coefficient = x = \frac{2\pi r}{\lambda}$$

r_1 = core radius

r_2 = shell radius

m_1 = refractive index in core

m_2 = refractive index in shell

Ref. Kaiser et. al., Computer in Physics, 1993

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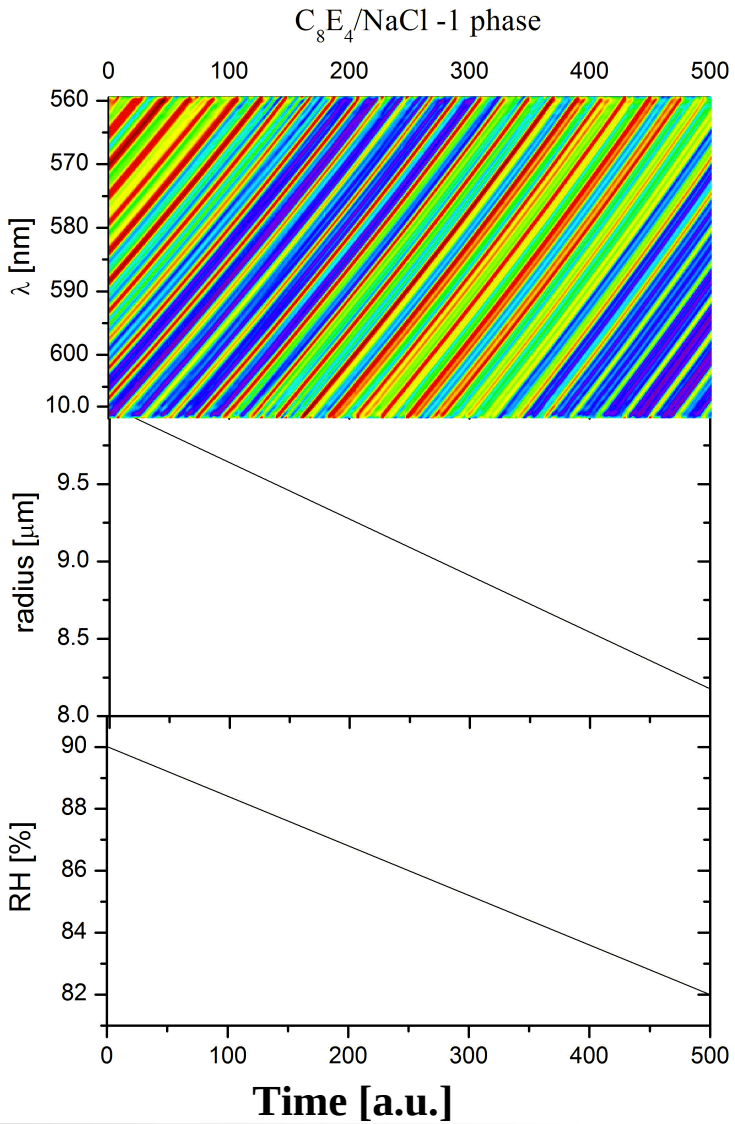
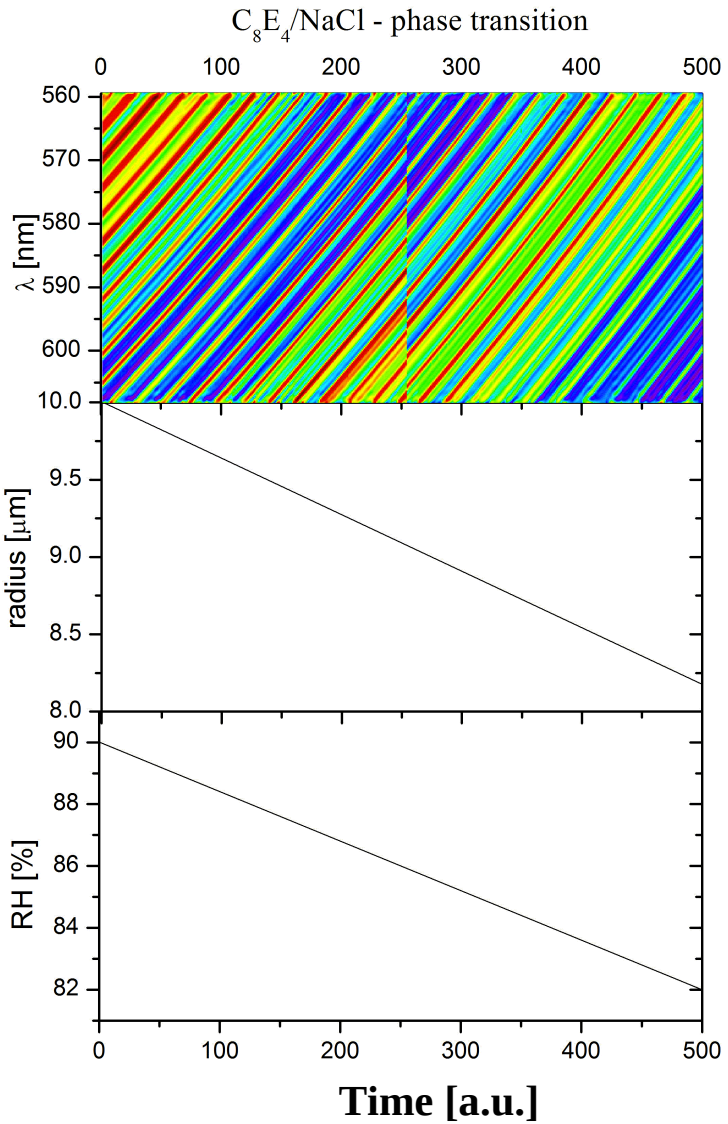
Phase transition modeling





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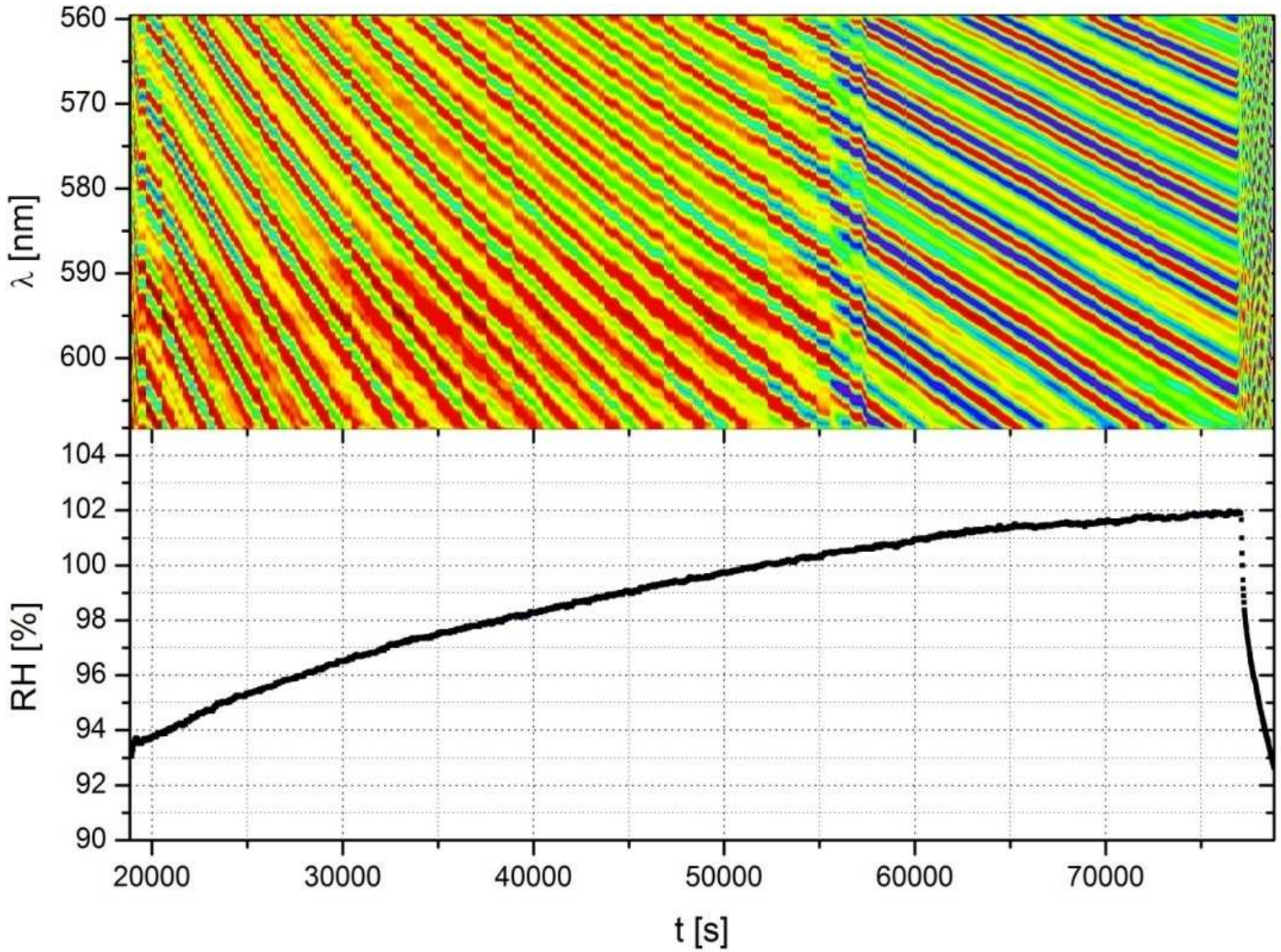
Preliminary Experiment from EDB of C_8E_4/NaCl/H_2O system



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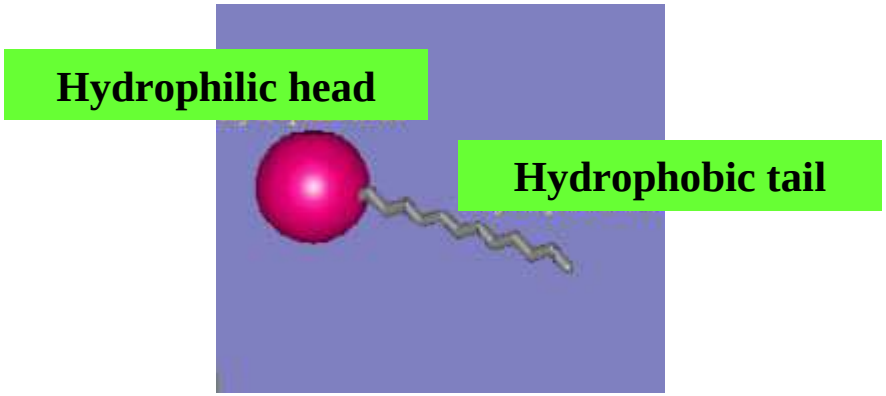
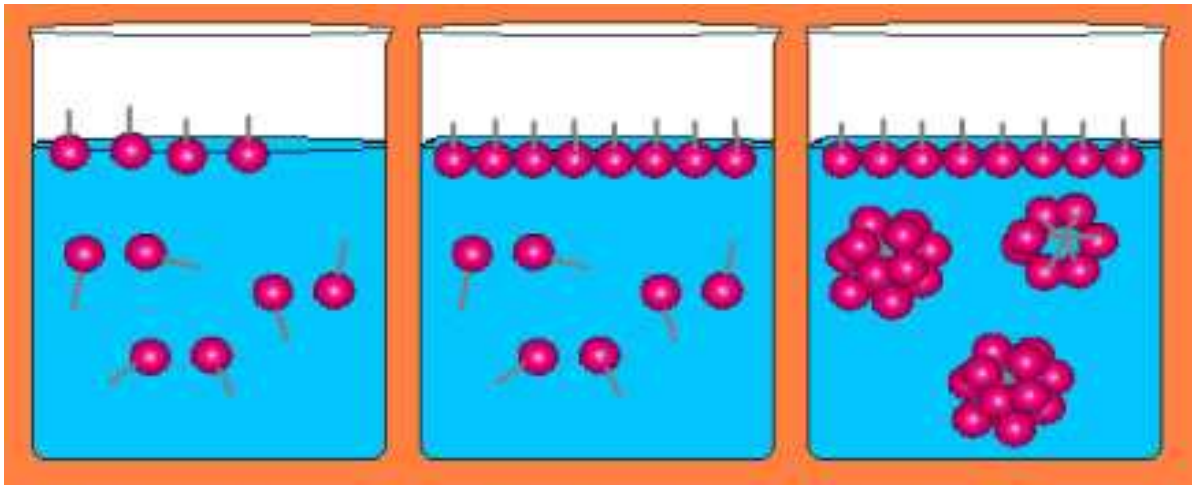
Micelles



Micelle formation



Low surfactant concentration	Higher concentration	Critical Micelle concentration

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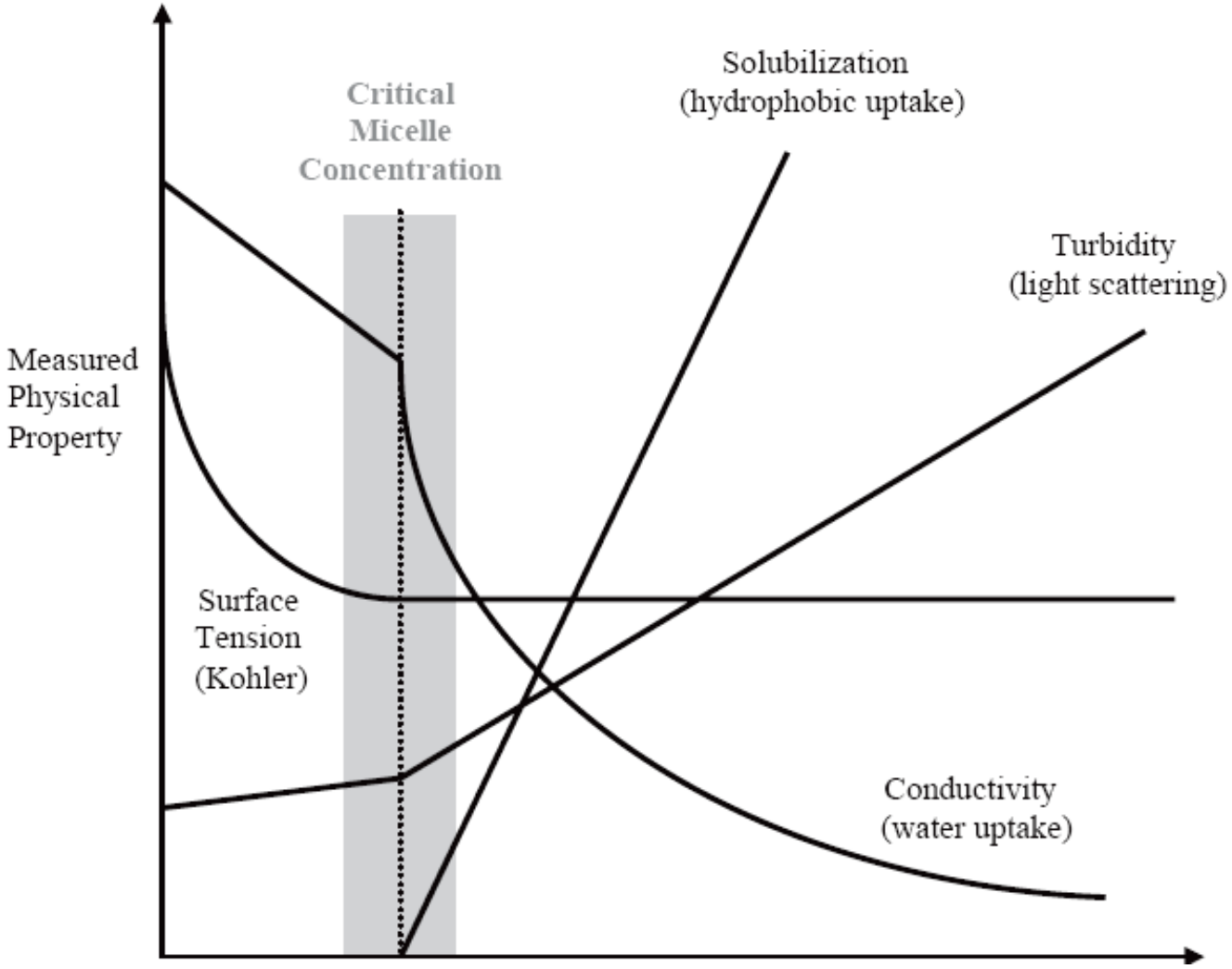
Critical Micelle Concentration (CMC)



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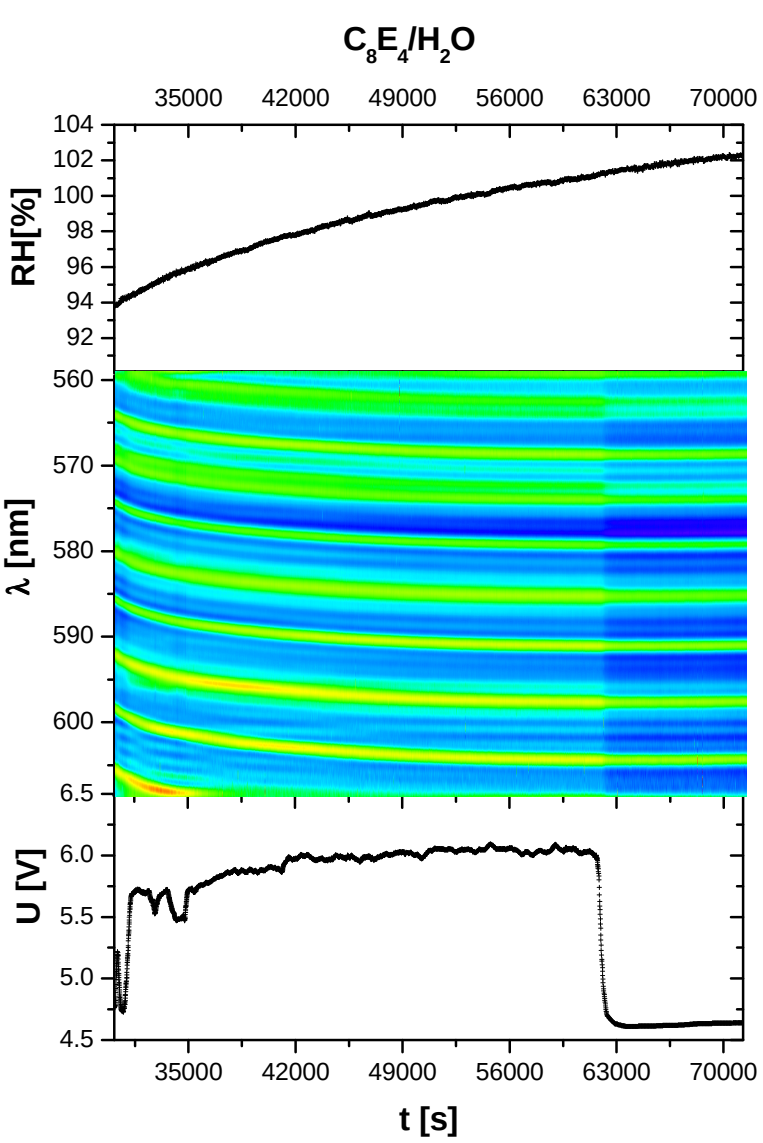
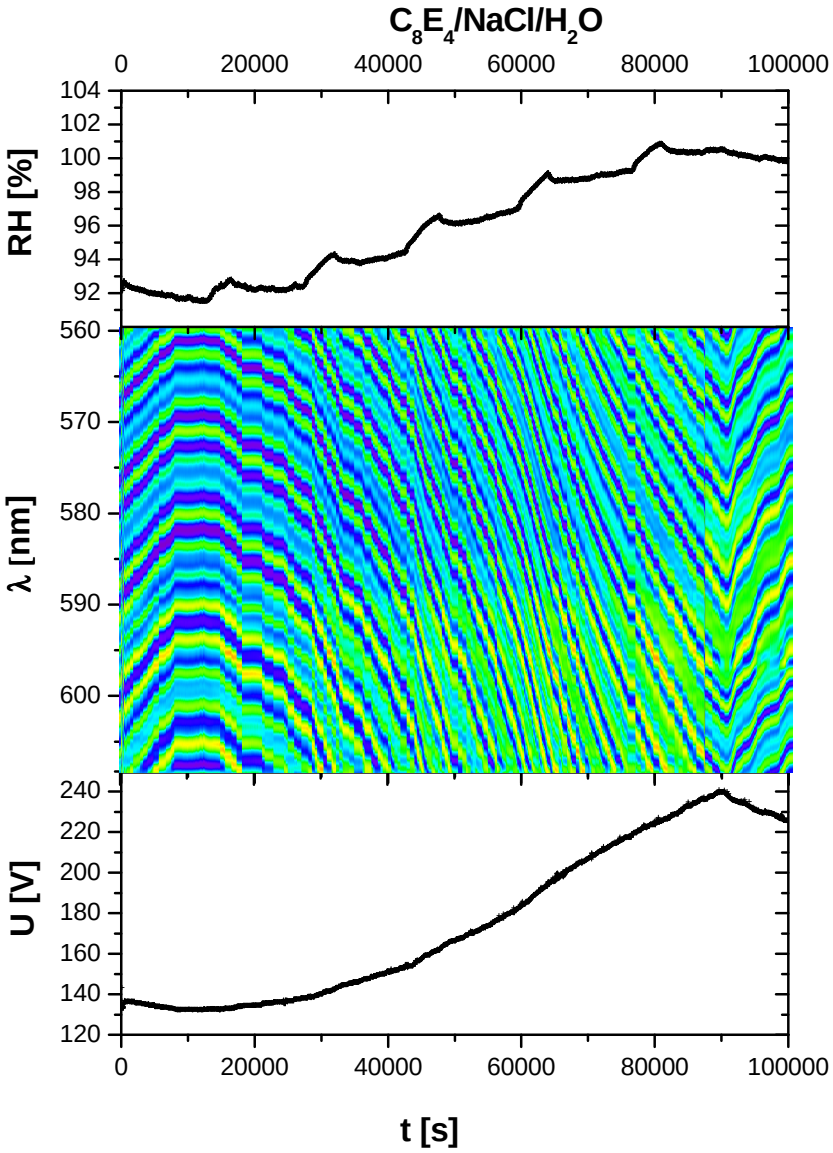
EDB Preliminary Experiment of $C_8E_4/NaCl/H_2O$ system





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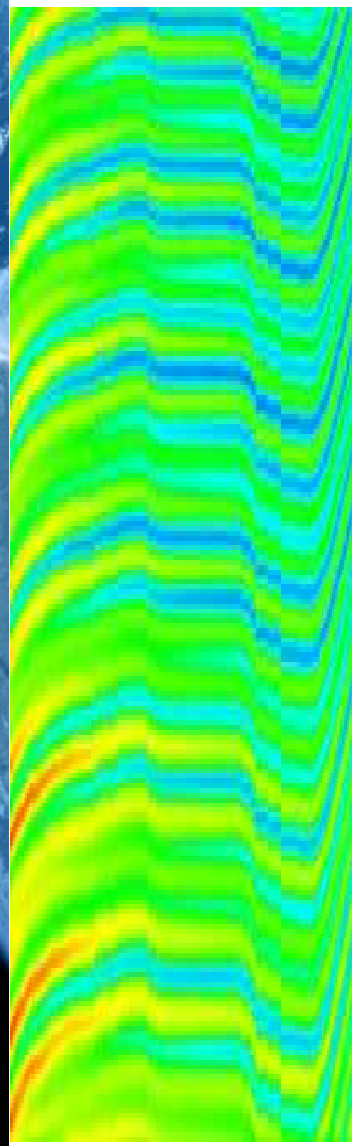
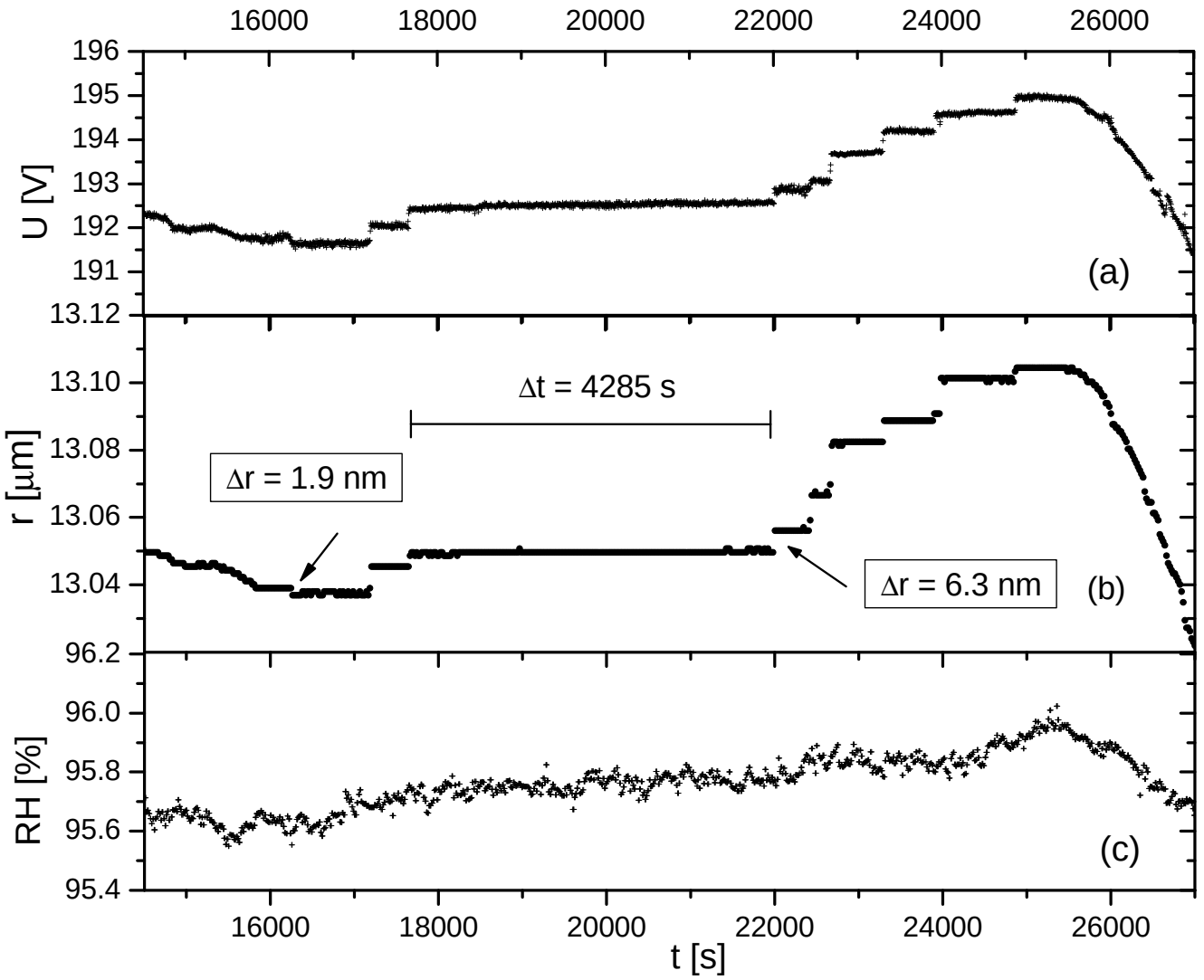
Step size analysis





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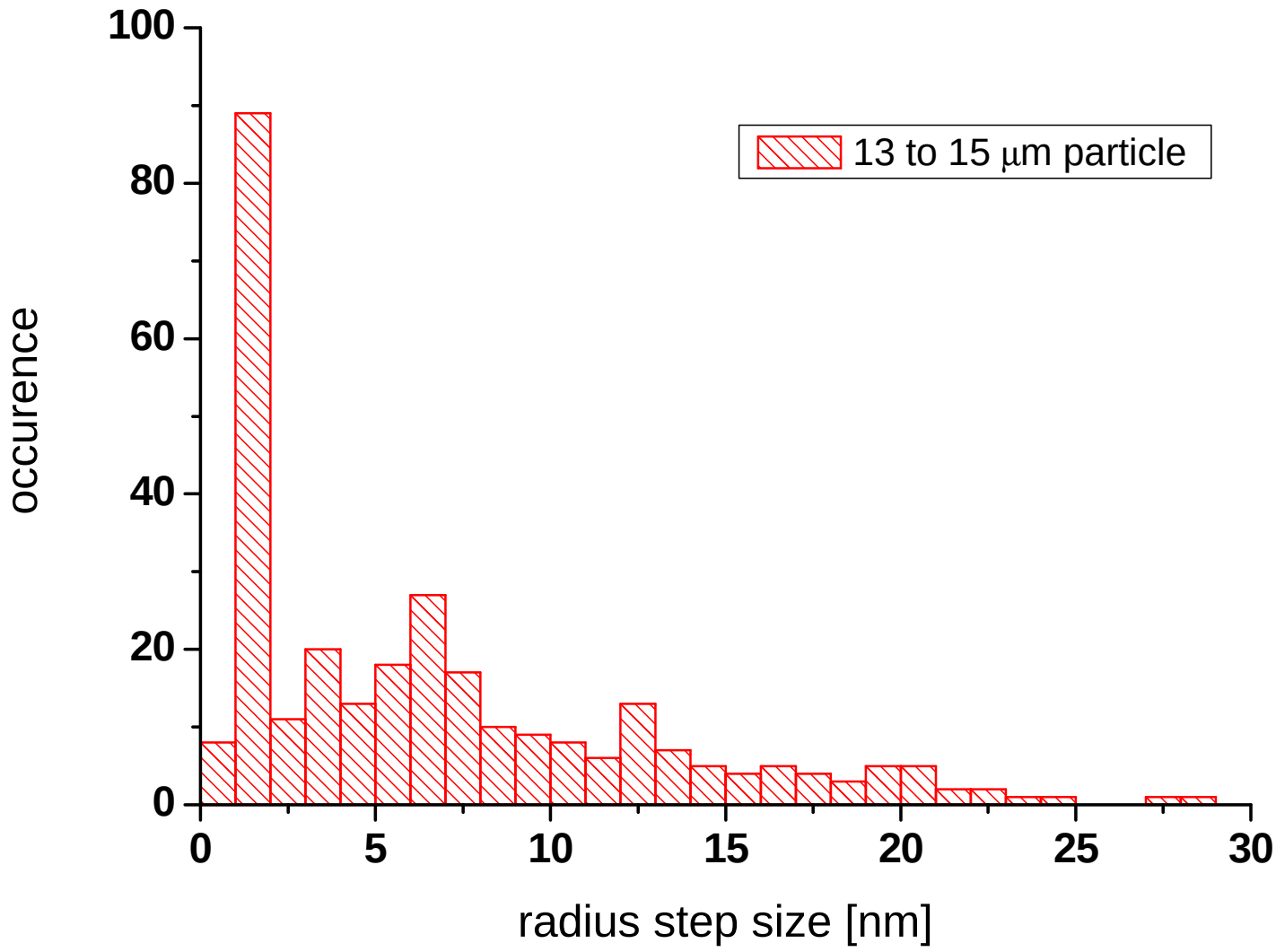
Radius Step Size



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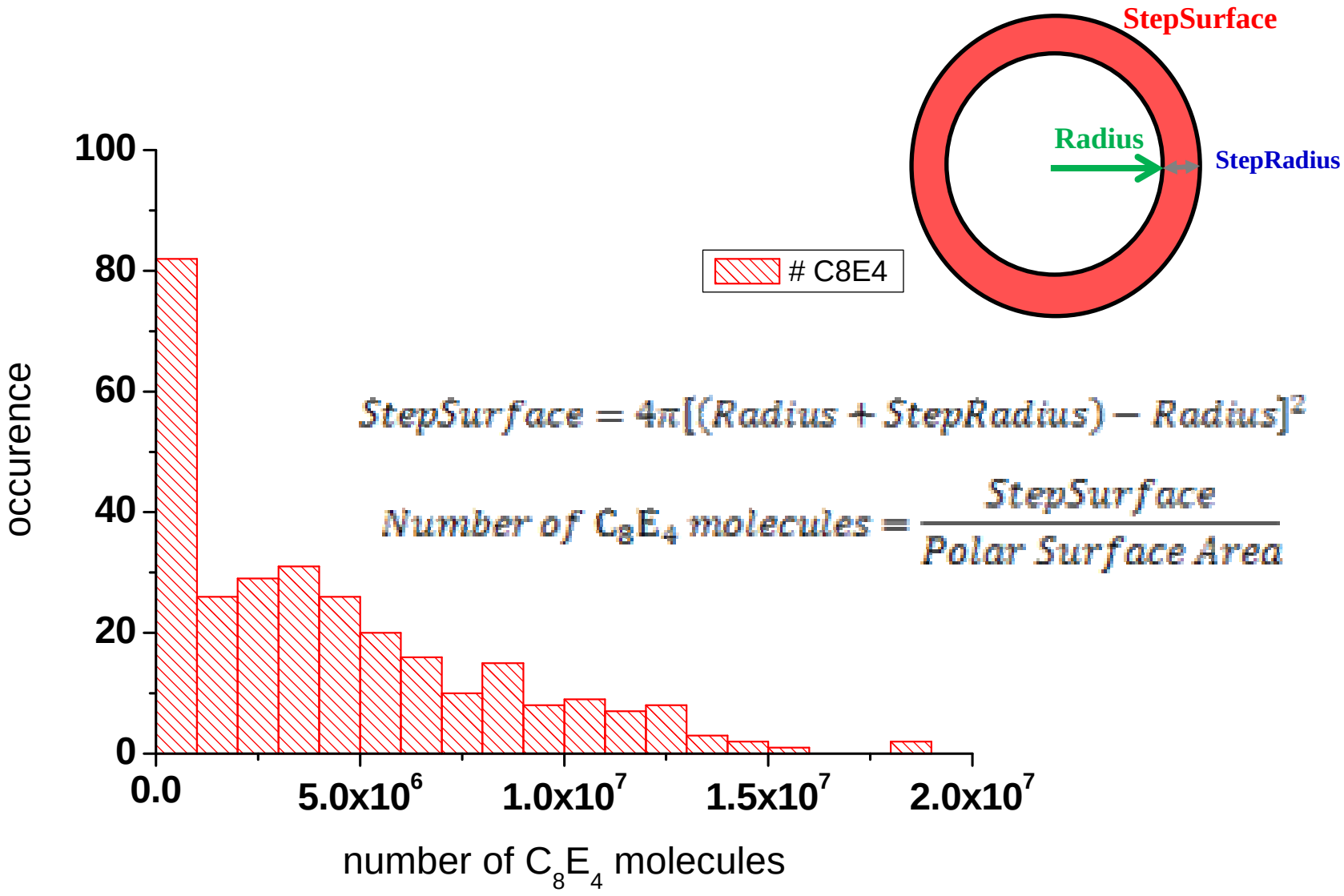
Number of C_8E_4 molecules



$$StepSurface = 4\pi[(Radius + StepRadius) - Radius]^2$$

$$Number\ of\ C_8E_4\ molecules = \frac{StepSurface}{Polar\ Surface\ Area}$$

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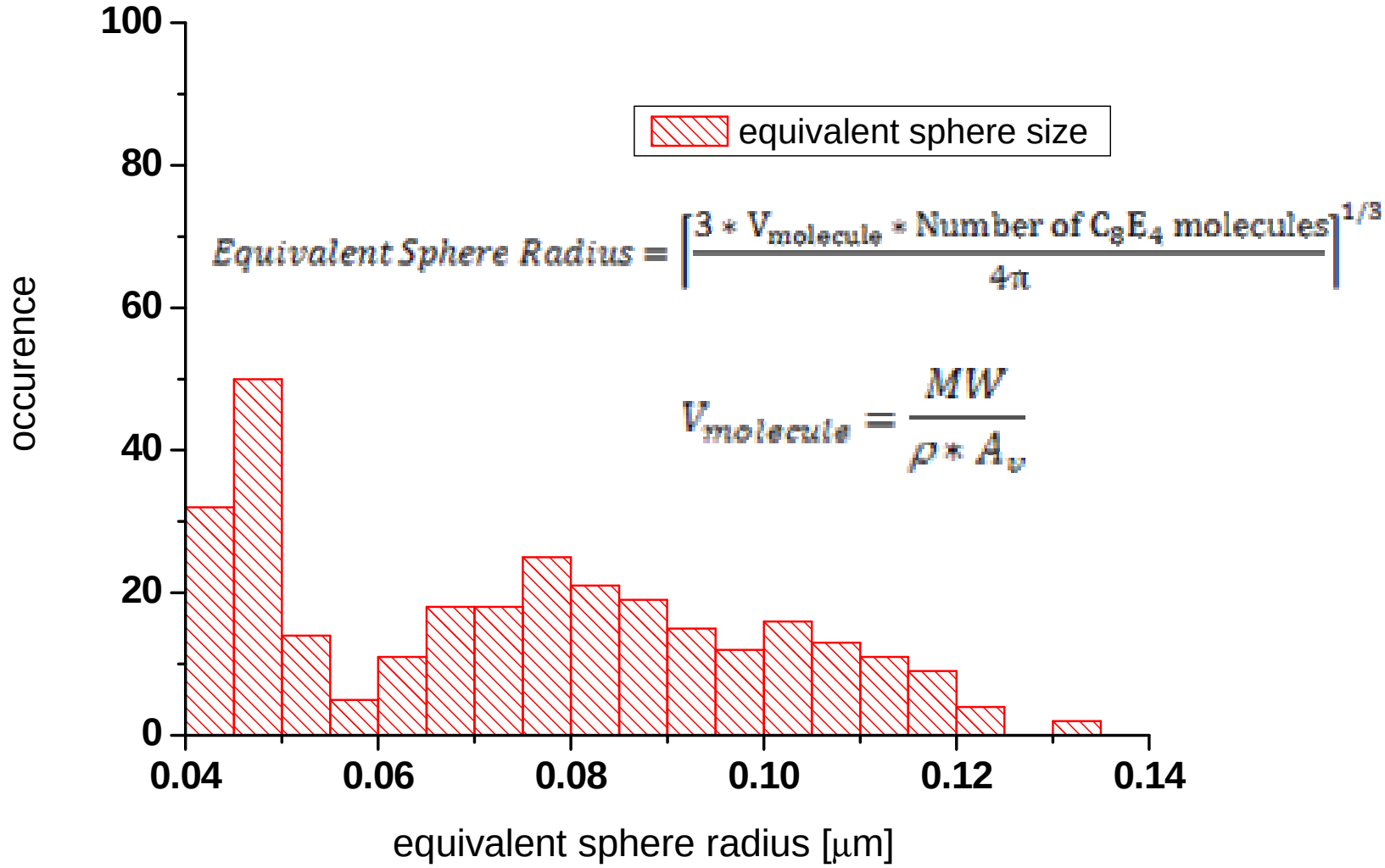
Equivalent Sphere Size



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Conclusion

- We speculate that the discontinuous, step like, growth is caused by disaggregation of a micelle needed to conserved the monolayer of surfactant molecules on the aqueous aerosol particle surface upon growing.

- We did not observe the discontinuous growth with binary C_8E_4/water particles.

- We intend to perform further experiments to investigate the influence of NaCl/C_8E_4 ratio on size distribution of micelles.

Take home messages

- When a liquid-liquid phase separation occurs, the inorganic salt is redistributed according to the solubility. If the organic substance is a surfactant, it will lower the surface tension and micelles may be formed if the concentration of the organic exceeds a certain limit.

- The discontinuous growth is caused by disaggregation of a micelle needed to conserved the monolayer of surfactant molecules on the aqueous aerosol particle surface upon growing.

- The concentration of salt in the particle might have an influence to size distribution of micelles.

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Reference:
Marcolli, C., Luo, B., &. Peter, T. (2004). *J. Phys. Chem. A*, 108, 2216-2224.
Zardini, A.A., Krieger, U.K., & Marcolli, C. (2006). *Optics Express*, 14, 6951-6962.

Thank you for your attention

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