Effects of methanol on crystallization of water in the deeply super cooled region

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INTRODUCTION

- *Anomalous properties of water, such as the density maximum at T=4 °C, might be explained using the presence of two liquid phases*
- *According to second critical-point hypothesis, it is important to uncover the properties of water in the deeply supercooled region*
- *distinct liquid phase is predicted to appear at ambient pressure*
- *liquid water cannot be supercooled below 235 K because of homogeneous nucleation*

GLASSY WATER PREPARATION TECHNIQUES

- *supercooled liquid water is made by heating glassy water*
- *Amorphous solid water (ASW) is formed by deposition of water vapor onto a cold substrate*
- *Hyperquenched glassy water (HGW) is vitrified liquid water at an extremely high rate of cooling*
- *Low-density amorphous (LDA) ice is prepared by pressure induced amorphization of hexagonal ice followed by decompression and heating*

In this paper

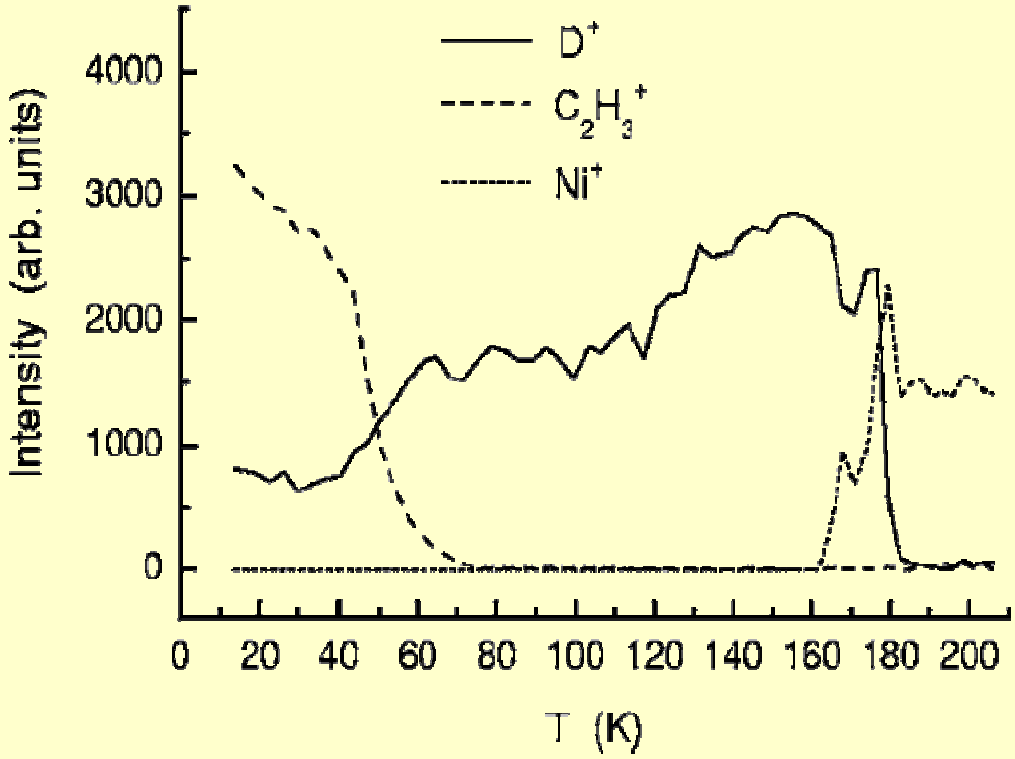
- *Interactions of water with butane and methanol molecules are investigated as a function of temperature using TPD, TOF-SIMS, and RAIRS*
- *kinetics of the glass-liquid transition and the crystallization of water with and without the adsorbed butane and methanol molecules*
- *How the crystal growth and desorption kinetics of butane are affected by methanol adsorbed on the surface*

TOF-SIMS

- *The TOF-SIMS and TPD experiments were performed in an UHV chamber with base pressure of less than $1X10^{-8}$ Pa*
- *The TOF-SIMS measurement was made by bombarding a sample surface (floated with a bias voltage of +500 V) with a pulsed He^+ beam (2.0 keV, approximately 10 pA/cm^2)*
- *The substrate was a Ni (111) surface, which was cleaned in the UHV chamber by heating to 1200 K using electron bombardment*
- *The coverage of the molecules was determined from the evolution curves of sputtered ion intensities as a function of exposure*
- *The TOF-SIMS and TPD spectra were recorded every 30 s at a ramping speed of 5 K min^{-1}*

RAIRS

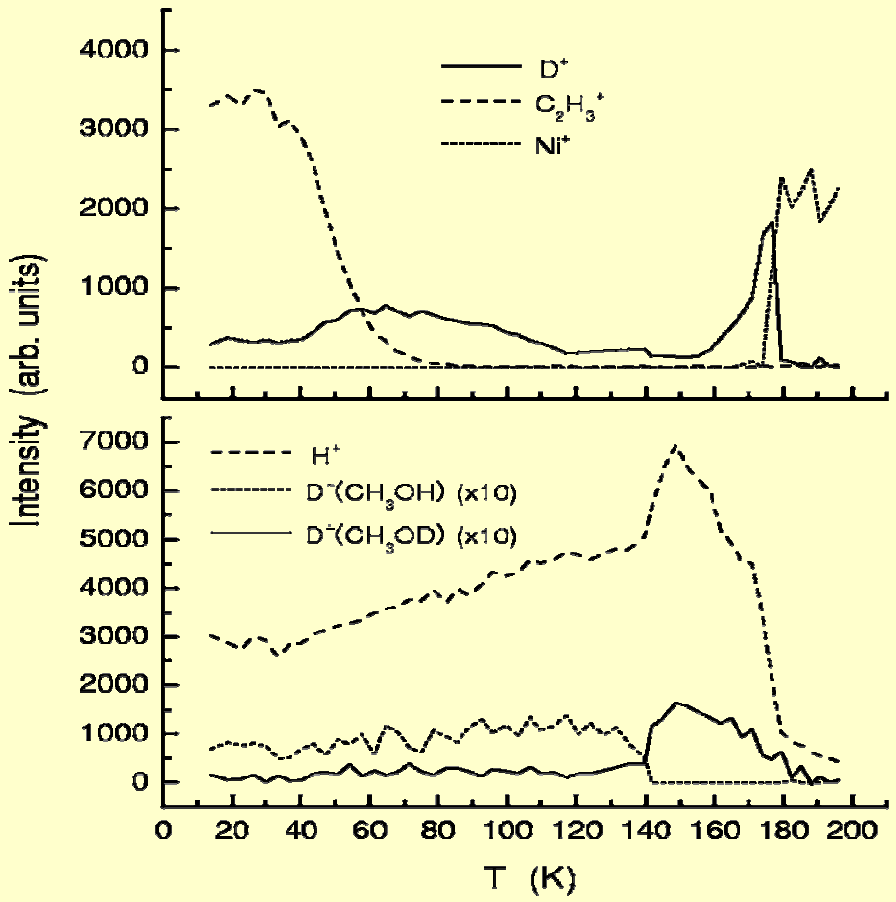
- *The RAIRS experiment was made in a UHV chamber with a base pressure of $3X10^{-8}$ Pa*
- *The infrared absorption spectra were taken using a Fourier transform infrared (FTIR) spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride detector*
- *The IR beam was reflected from a gold film deposited on a mirror-finished Ni plate with a grazing angle of 5°*
- *The substrate was cooled to 85 K using liquid nitrogen*
- *The spectra were taken over the wave number range of 400-4000 cm^{-1} with an 8 cm^{-1} resolution*
- *The temperature was increased at the same ramping speed as that used for TOF-SIMS and TPD*
- *50 spectra were taken continually at temperatures of 90-200 K*



TOF-SIMS intensities of typical secondary ions sputtered from the butane-adsorbed D_2O film as a function of temperature

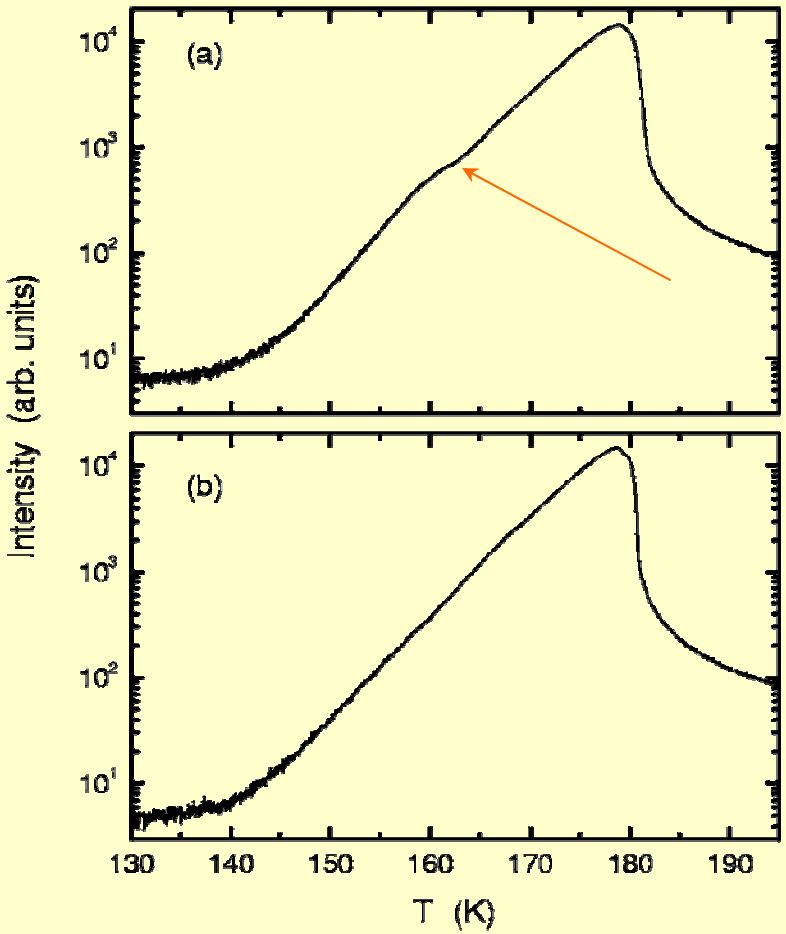
40 ML of the D_2O molecules were deposited on the Ni (111) Substrate at 15 K and then heated at 100 K. 1 ML of C_4H_{10} molecules were adsorbed on it at 15 K. The temperature was increased at a rate of 5 K min^{-1}

- ***C_4H_{10} molecules disappear completely from the surface > 80 K,This is due to dissolution of butane into the bulk of the D_2O film rather than Desorption***
- ***The phenomenon is caused by pores or hydrogen-bond imperfections that are present in the ASW films***
- ***phase transition of water takes place at around 165 K prior to the film evaporation***
- ***Identical results are obtained for pure ASW films, indicating that butane has negligible effects on the properties of water***



TOF-SIMS intensities of typical secondary ions sputtered from the D_2O (40 ML) film co-adsorbed with the C_4H_{10} (1 ML) and CH_3OH (2 ML) molecules as a function of temperature

- ***Methanol remains on the D_2O film surface up to the film evaporation temperature***
- ***The absence of the hump in the sputtered Ni^+ intensity at 165 K, indicating that film de-wetting is quenched by methanol***
- ***The absence of the H^+ (CH_3OH) ion shows that all the CH_3OH molecules form hydrogen bonds with the D_2O molecules during the pre annealing process up to 100 K***
- ***The H^+ intensity increases at temperatures > 140 K, suggesting that the methanol molecules change their orientation at this temperature***
- ***The surfactant effect of methanol that reduces the surface tension is the main reason for quenching the morphological change of the fluidized water film***

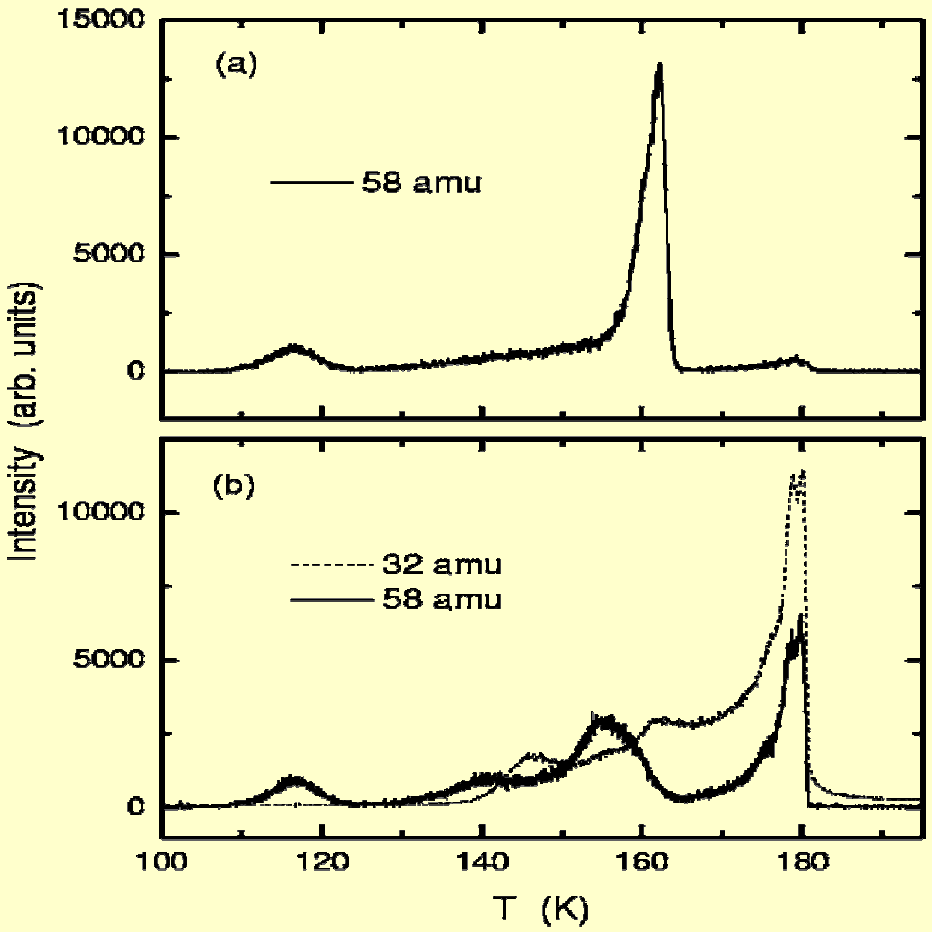


TPD spectra of the D_2O molecules (20 amu) desorbed from the

(a) C_4H_{10} (1 ML)/D_2O (40 ML)

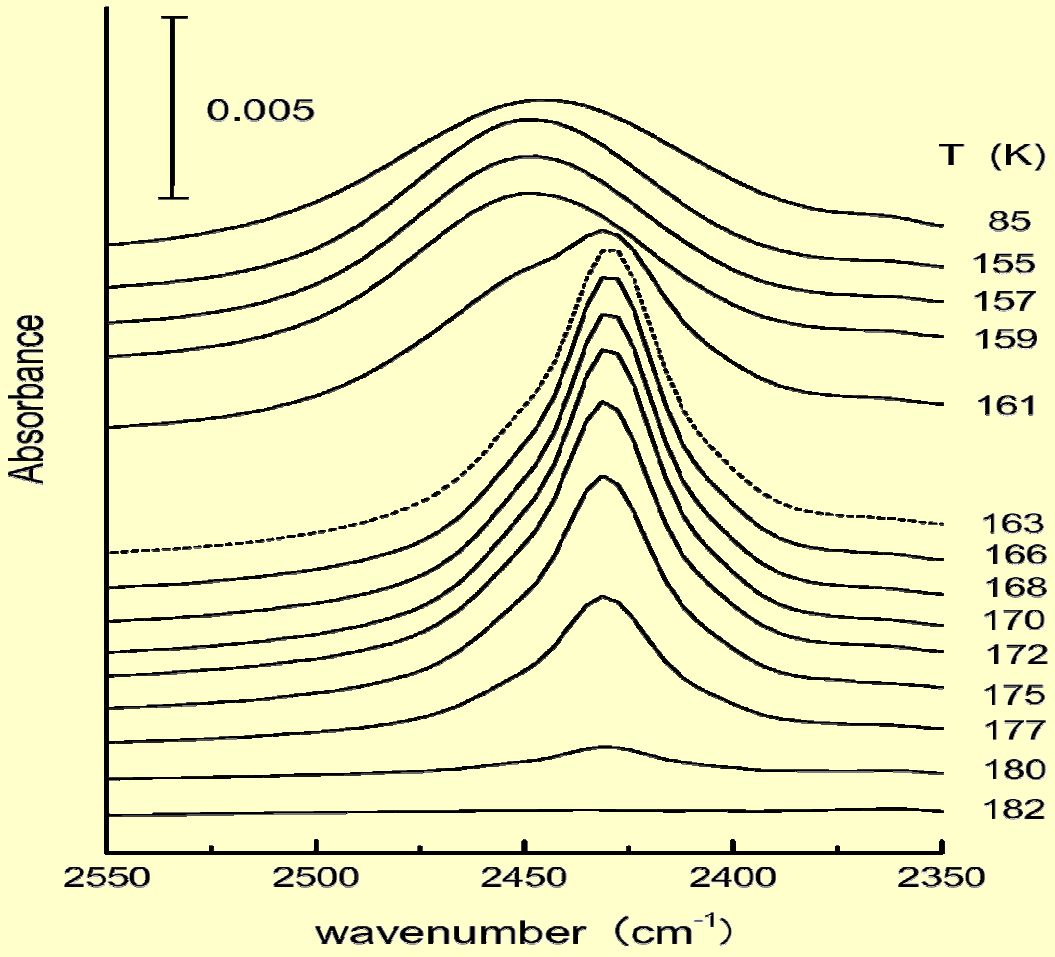
(b) CH_3OH (2 ML) / C_4H_{10} (1ML)/D2O (40 ML) films

- *The Desorption rate of the D_2O molecules decreases abruptly at around 160-165 K*
- *The hump at 165 K disappears when methanol is present on the surface, which is related to the change in film morphology*
- *Abrupt crystallization of water occurs because the Desorption rate of H_2O molecules from the crystalline ice is inferred to be orders of magnitude smaller than that from the ASW*
- *This phenomenon cannot be assigned uniquely to crystallization because the assumption of the layer-by-layer Desorption from the uniform film surface is not valid for the pure ASW film*



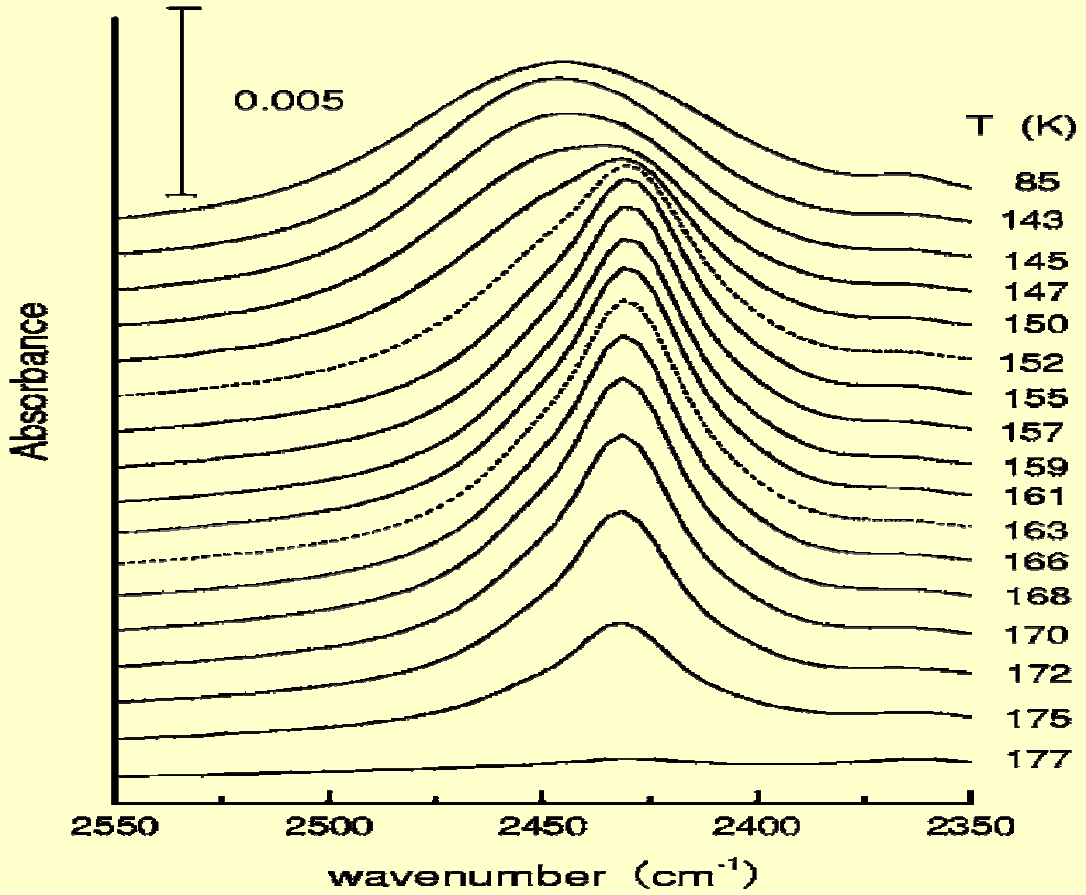
TPD spectra of the C_4H_{10} (58 amu) and CH_3OD (32 amu for the CH_2OD^+ ion) molecules desorbed from (a) C_4H_{10} (1ML)/D_2O (40 ML) (b) CH_3OH (2ML)/C_4H_{10} (1 ML)/D_2O (40 ML)

- *The peak at 117 K comes from the weakly bound butane molecules incorporated in the shallow subsurface site and the peak at 162 K is ascribable to hydrates of butane in the bulk*
- *The high temperature cutoff of the main peak (163 K) corresponds to the temperature for the simultaneous changes in the Desorption rate of the D_2O molecules and the film morphology*
- *The TPD spectrum of methanol exhibits a broad structure, together with three peaks at 146, 162, and 180 K*
- *The Desorption kinetics of the butane and methanol molecules appears to be mutually correlated, as inferred from the alternative emergence of the peaks with increasing temperature*



RAIR spectra in the OD stretching region of HOD (10 mol %) in H2O as a function of temperature,40 ML of water molecules were deposited on the Au film at 85 K

- ***precise assignment of the band is difficult because of peak broadening which is due to anharmonicity of the vibrations generated by extensive hydrogen bonding***
- ***The band at 85 K exhibits a maximum at 2453 cm^{-1} The red shift and narrowing of the spectra is due to crystallization***
- ***This result shows that spontaneous nucleation occurs abruptly near 160-165 K***
- ***The spectra after crystallization are asymmetric***



RAIR spectra in the OD stretching region of HOD (10 mol %) in H2O as a function of temperature,2 ML Of Butanol was adsorbed on 40 ML water film

- ***The shape of the band changes at around 150 K because of the crystallization***
- ***The band is asymmetric suggesting the coexistence of the crystal and amorphous phases***
- ***The crystallization temperature is fixed at around 152 K over the methanol coverage of 2-20 ML***
- ***The kinetics of crystallization is affected strongly by the specific additives that are incorporated in the bulk of the water films***

CONCLUSION

- ***Adsorption of alcohols with a longer aliphatic chain, such as ethanol and 1-Butanol, does not lower the crystallization temperature of water although they act as a surfactant to quench the film dewetting***
- ***The lower solubility of these alcohols in water is thought to be responsible for this behavior.***
- ***A remarkable effect of adsorbed methanol is the lowering of the crystallization temperature from 165 to 152 K***
- ***No crystals are formed in the LDL phase of the ASW film because of the absence of nuclei***
- ***The crystallization of water is incomplete both with and without methanol***
- ***Almost complete dehydration of butane up to 165 K is related to the liquid-liquid transition rather than the crystallization***

- ***Ice (Ic) is inferred to be equilibrated with the viscous liquid phase (probably LDL), as evidenced by the overlapping of the broad IR absorption band***
- ***Self-diffusion of the water molecules (136 K) and de wetting of the film (165 K), strongly suggests that the glass-liquid transition of water is a two-step process***
- ***Distinct LDL phase emerges from LDA (ASW) at temperatures greater than 136 K, then the LDL phase transforms into supercooled liquid water (LDL+HDL) at approximately 165 K***

RELAVANCE

- *crystallization quenching molecules can be incorporated in to ice and see their effect on different forms of ice*
- *Kinetics of the desorbing molecules can be analyzed*
- *rough estimation of number of alcohol molecules that is adsorbed on the surface can be studied by TPD in which the number of adsorbates can be directly related to the area under the TPD curve*
- *Phase separation can be analyzed between ASW and alcohols as well as any structural transformation that occurs can also be studied*