

SANS法で観測する 混合溶液のナノ不均一性

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Mixtures of Water and Organic Solvents

- Mixtures of water and water-miscible organic solvents, such as acetonitrile and fluoroalcohol, are often used as reaction and separation fields.
- They are inhomogeneously mixed each other; water clusters and organic solvent clusters are formed in the mixtures.
- Thus, phase separation of the mixtures may occur with adding solute and varying temperature.

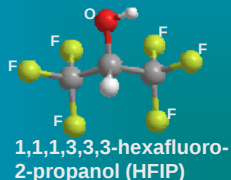
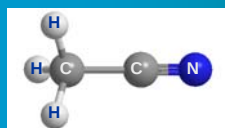
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Present investigation

- Phase separation of acetonitrile-water mixtures by addition of alkali chloride salts, such as LiCl, NaCl, and KCl.
- Phase separation of HFIP-water mixtures by addition of organic solute, amides.
- SANS, LAXS, and MD experiments were made to clarify the mechanism of phase separation.

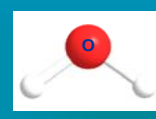
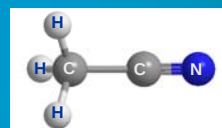


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Alkali Chloride-Induced Phase Separation of Acetonitrile-Water Mixtures



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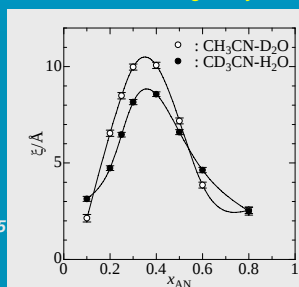
Mixing State of Acetonitrile-Water Binary Mixtures

At the molecular level, acetonitrile and water molecules are heterogeneously mixed each other; **microheterogeneity occurs in the mixtures.**

SANS Experiments using
SANS-U at JAEA.

The UCST for acetonitrile-water mixtures is -1°C at $x_{\text{AN}} = 0.38$.

T.Takamuku et al., J.P.C.B, 2001, 105 6236.



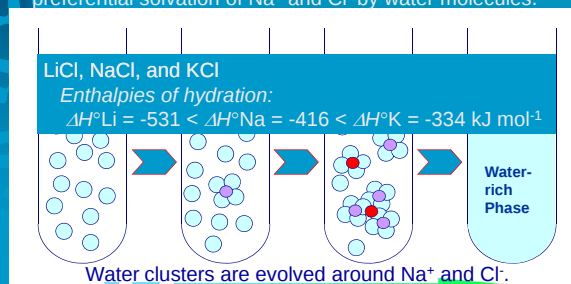
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NaCl-induced phase separation of AN-water

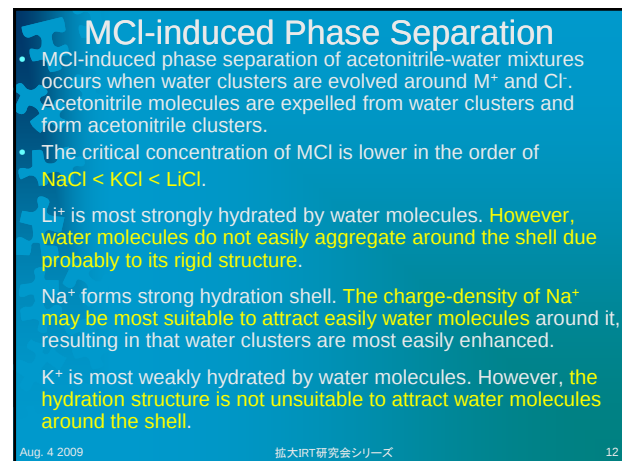
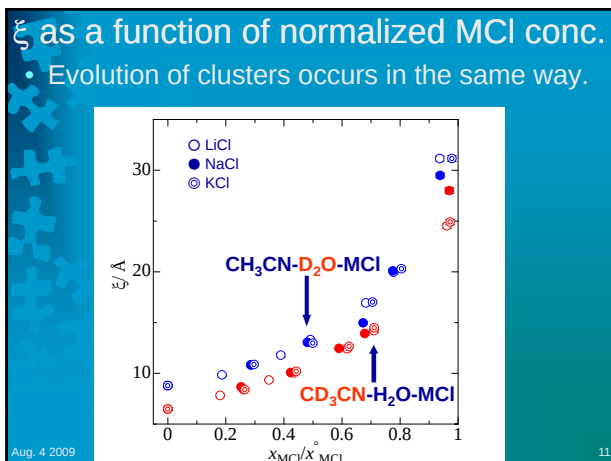
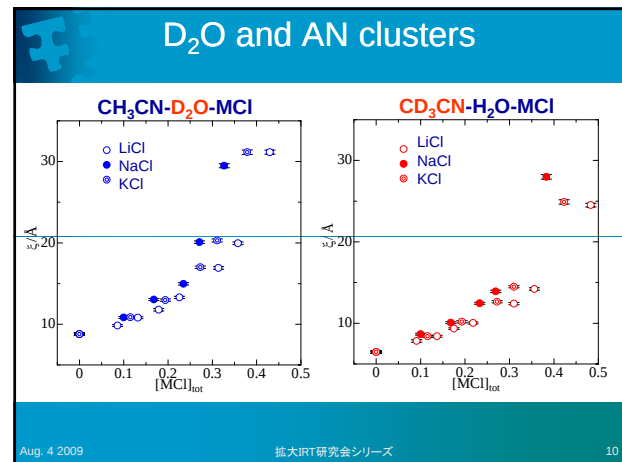
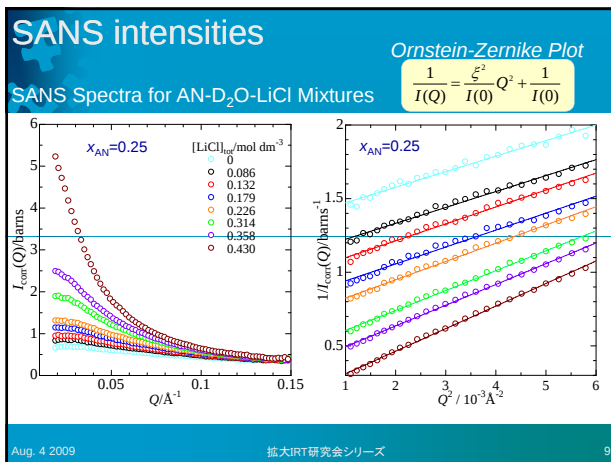
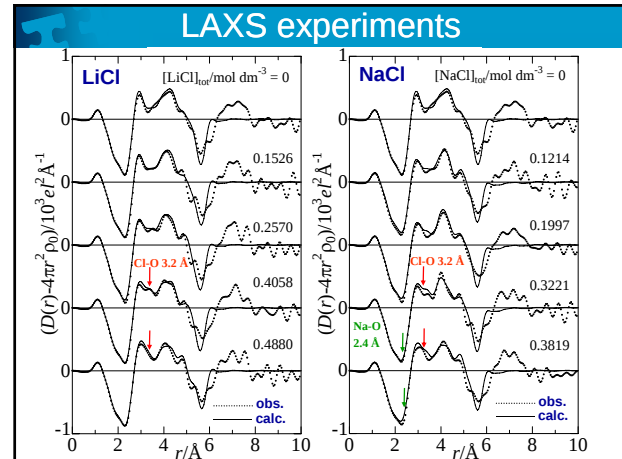
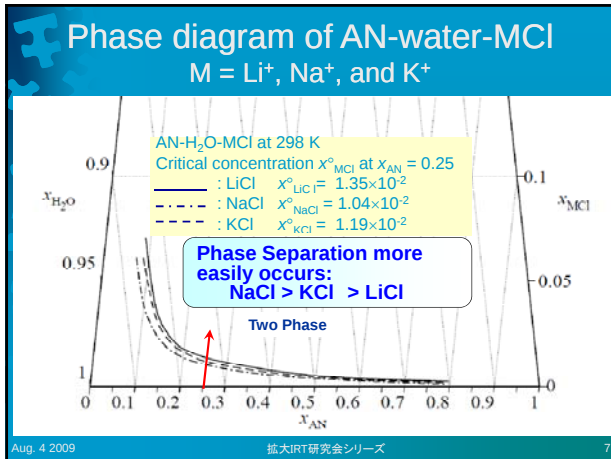
- Phase separation occurs when the microheterogeneity is further enhanced with increasing NaCl concentration due to preferential solvation of Na^+ and Cl^- by water molecules.



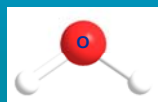
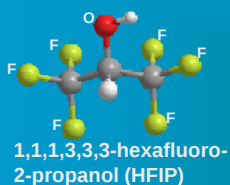
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Amide-Induced Phase Separation of HFIP-Water Mixtures

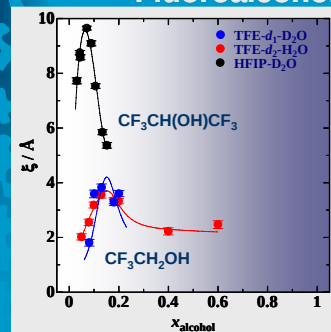


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Inhomogeneous mixing of Fluoroalcohol-water



- Fluoroalcohols, such as TFE and HFIP, are inhomogeneously mixed with water.
- The inhomogeneity is much higher than aliphatic alcohol-water systems.
- Fluoroalcohol clusters and water clusters are formed in the mixtures.

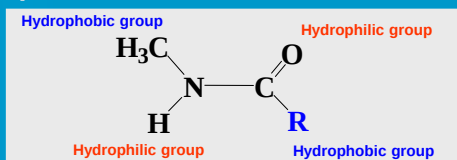
TFE-Water: T. Takamuku et al., J. Phys. Chem. A, 109, 7667 (2005).
HFIP-Water: K. Yoshida et al., J. Chem. Phys., 119, 6132 (2003).

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Amphiphilic amides in HFIP-water mixtures



Amides

- N*-methylformamide (NMF) R = H
N-methylacetamide (NMA) R = CH₃
N-methylpropionamide (NMP) R = CH₂CH₃
N,N-dimethylformamide (DMF) R = H

- Phase separation of HFIP-water mixtures occurs with increasing amide content.

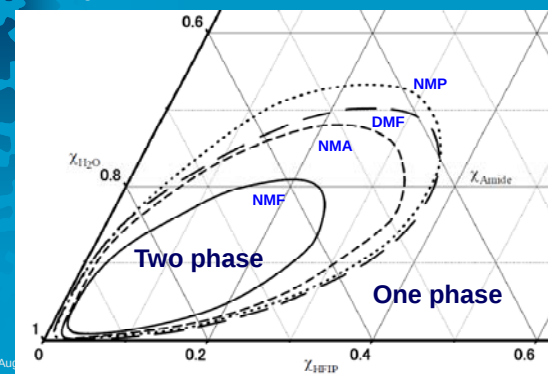
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Phase diagrams for Amide-HFIP-water at 25°C

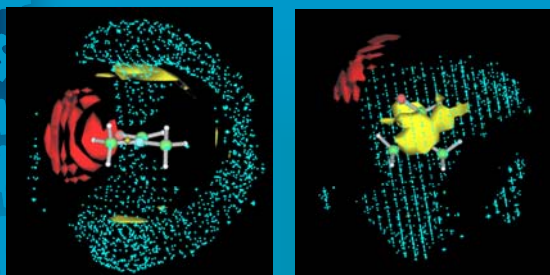
- Cyclic region of phase separation.
- The region is wider in the order of **NMF < NMA < DMF < NMP**.



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MD simulation on Solvation for DMF



Red: Water Oxygen, Blue: HFIP Carbon, Yellow: HFIP Fluorine

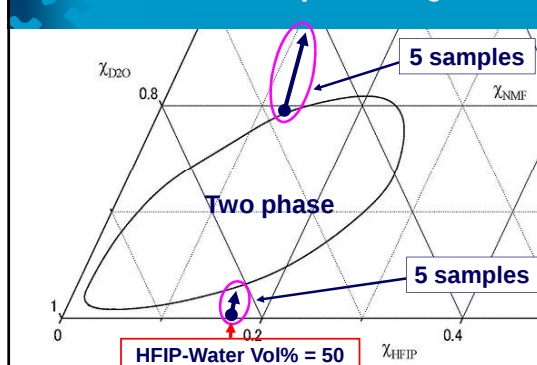
- DMF molecule is surrounded by the fluoroalkyl group of HFIP molecules.

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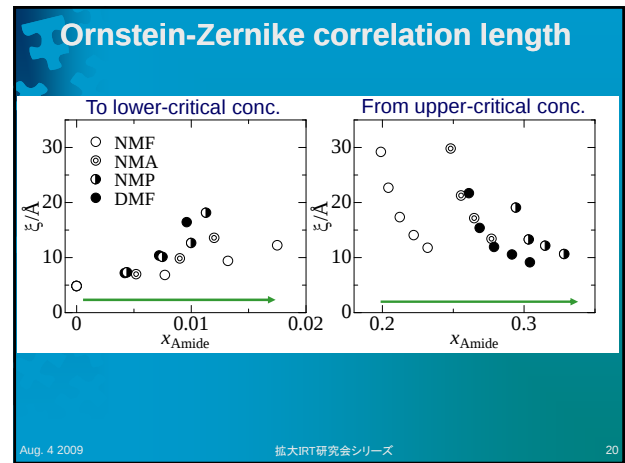
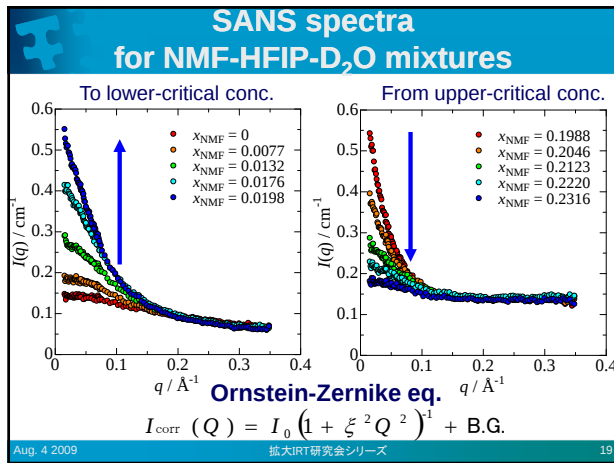
SANS experiments in accordance with phase diagram at 25°C



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Mechanism of amide-induced phase separation

- The lower-critical concentration**
The hydrophobic moiety of amide molecule is surrounded by HFIP molecules, leading to phase separation due to enhancement of HFIP clusters.

- The upper-critical concentration**
Hydrogen bonds between amide and water molecules are strengthened due to the decrease in HFIP content, returning to one phase solution.

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