Formation, Structures, and Encapsulation Properties of Multiply Charged NaAOT Micellar Assemblies in The Gas Phase

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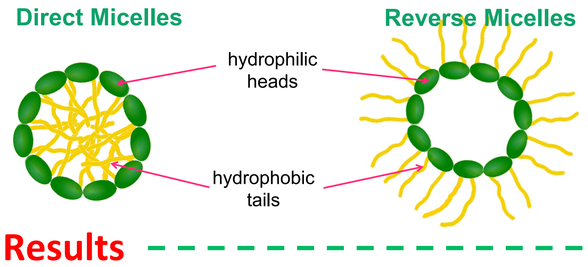
I. Introduction

Motivation

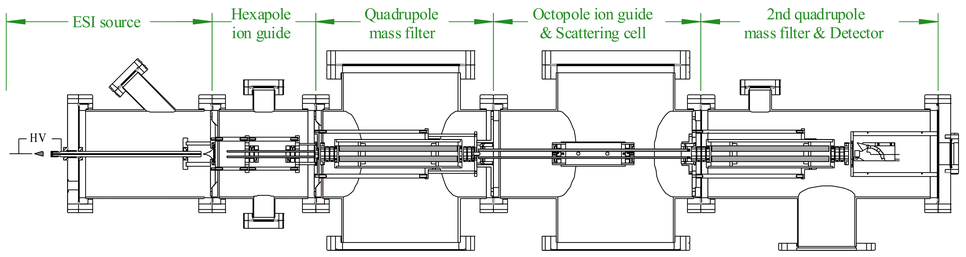
Generate gas-phase micelles in laboratory, and use them as nano-sized carriers/reactors to study chemistry of biomolecules in gas-phase membrane-mimetic environments.

Two distinct micellar structures

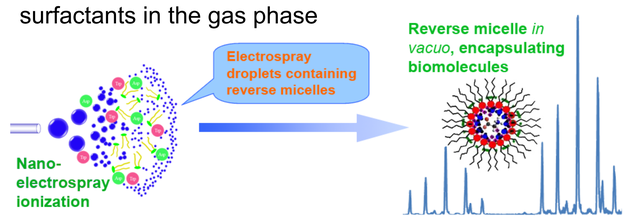


II. Apparatus & Methods

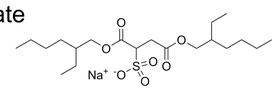
Home-made ESI Guided-Ion-Beam Tandem Quadrupole Mass Spectrometer



ESI of surfactant solution, followed by self-assembling of surfactants in the gas phase



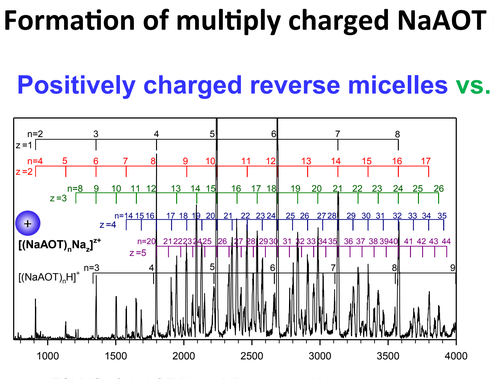
Surfactant: NaAOT sodium bis(2-ethylhexyl) sulfosuccinate



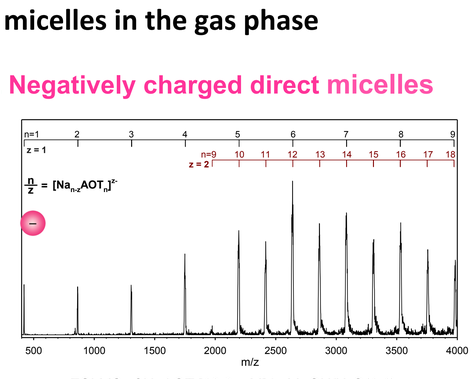
III. Results

❶ Formation of multiply charged NaAOT micelles in the gas phase

Positively charged reverse micelles vs. Negatively charged direct micelles



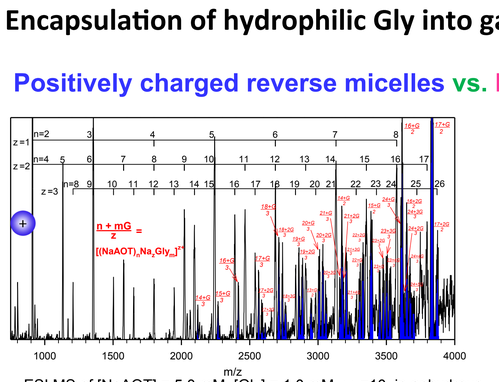
ESI MS of NaAOT [5.0 mM], ω_0=10 in Hexane



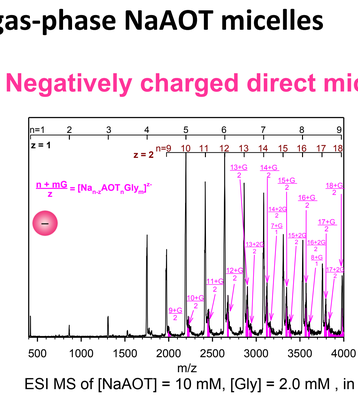
ESI MS of NaAOT [10.0 mM] in MeOH/H_2O(1:1)

❷ Encapsulation of hydrophilic Gly into gas-phase NaAOT micelles

Positively charged reverse micelles vs. Negatively charged direct micelles

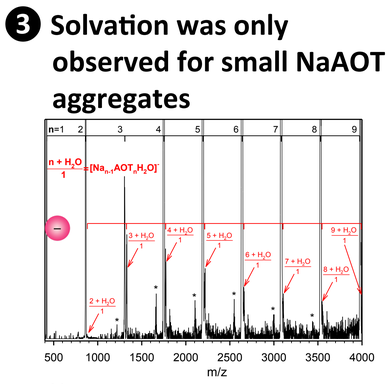


ESI MS of [NaAOT] = 5.0 mM, [Gly] = 1.0 mM, ω_0=10, in anhydrous hexane



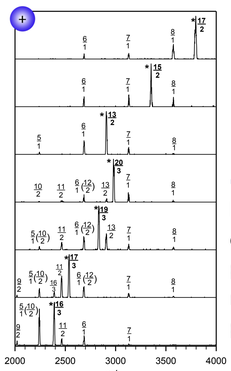
ESI MS of [NaAOT] = 10 mM, [Gly] = 2.0 mM , in MeOH/H_2O

❸ Solvation was only observed for small NaAOT aggregates



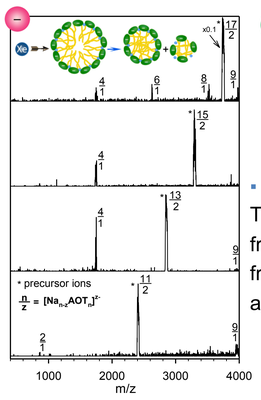
Note:
No solvation was observed in large positively & negatively charged NaAOT micelles

Collision-induced-dissociation (CID) of mass-selected micellar ions with Xe (E_{col} = 1.0 eV)



- **Symmetric fission**

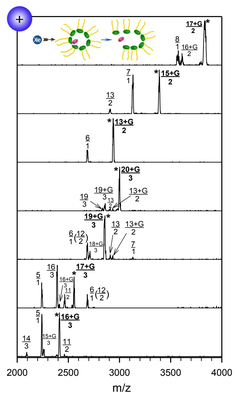
Major CID channels correspond to divisions of precursor ions into two nearly equally-sized product ions



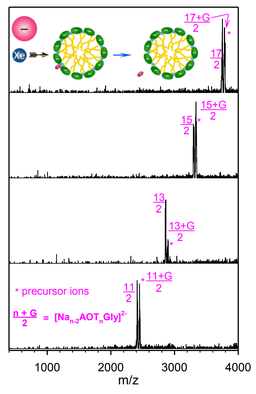
- **Asymmetric fission**

The sizes of two fragment ions produced from a negative NaAOT aggregate differ greatly

CID of mass-selected occupied micellar ions with Xe (E_{col}=1.0eV)



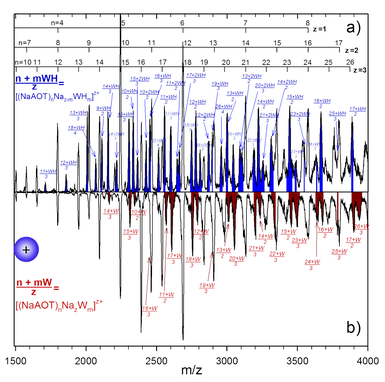
- CID leads to breakdown of micellar aggregates, in order to eject encapsulated Gly
- Consistent with a reverse micellar structure



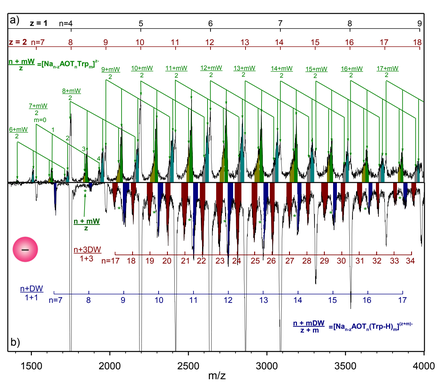
- CID leads to stripping of Gly, and only Gly, off the micellar aggregates
- Suggest a direct micellar structure and Gly is adsorbed to the outer surface

❹ Encapsulation of hydrophobic Trp and protonated/deprotonated Trp in gas-phase AOT micelles

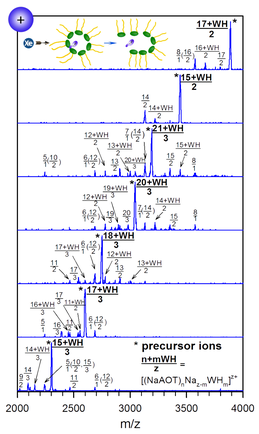
Encapsulation of neutral & protonated Trp in positively charged NaAOT reverse micelles



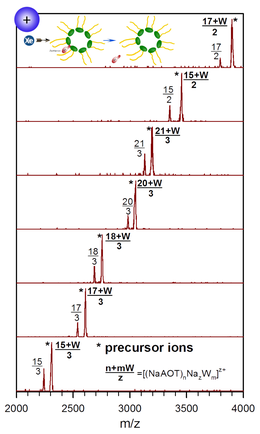
Incorporation of neutral & deprotonated Trp into negatively charged NaAOT direct micelles



CID of mass-selected Trp-encapsulated NaAOT micelles

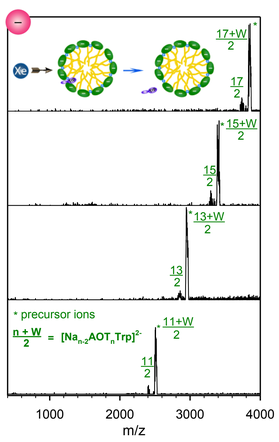


CID of $TrpH^+$-containing positively charged NaAOT reverse micelles lead to breakdown of whole micellar structure



CID of neutral Trp-containing positively charged NaAOT reverse micelles lead to stripping of only Trp off micellar aggregates **(Different than Gly-containing reverse micelles)**

VS.

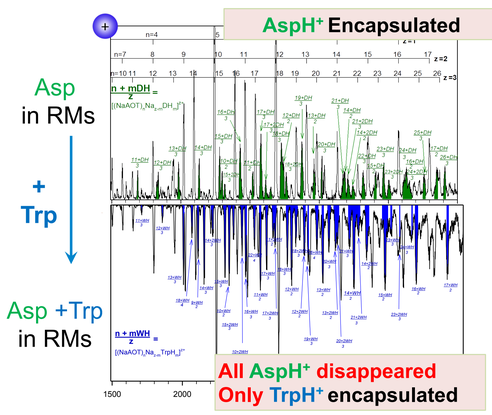


CID of neutral Trp-containing negatively charged NaAOT micelles lead to stripping of Trp off the micellar aggregates **(Similar as Gly-containing direct micelles)**

- CID results suggest different site locations of Trp, $TrpH^+$, Gly in positively and negatively charged NaAOT micelles, as indicated by cartoons inserted in the figures.
- Direct evidence for gas-phase micellar structures.

❺ Selective encapsulation of different AAs by positively charged NaAOT reverse micelles

Aspartic Acid vs. Tryptophan



Fundamentals of selectivity

❖ Selectivity reflects a competition between electrostatic and hydrophobic forces

Aspartic acid (D)	Tryptophan (W)
pI = 2.8*	pI = 5.9

❖ Amino acid with a higher pI exists in protonated form and has a larger affinity with AOT^-.

❖ Preference for encapsulation within micellar core increases in ascending order of amino acid pI values (*adopted from aqueous solution, just as a guide).

IV. Conclusions

❖ **NaAOT surfactants are able to self-assemble into highly-ordered micellar structures in the gas phase**

❖ **Charge state governs micellar structure in the gas phase. Positively charged aggregates form a reverse micelle-like structure, while negatively charged aggregates adopt a direct micelle-like structure.**

❖ **Amino acids can be selectively encapsulated and transported by NaAOT direct and reverse micelles.**

Applications

Gas-phase NaAOT micelles may act as

1) **nano-sized vehicles for transport of non-volatile biomolecules into the gas phase,**
2) **nano-sized reactors for investigating single biomolecules encapsulation in gas-phase bio-membrane mimetic systems.**

Related Publications:

1) Y. Fang, A. Bennett, and J. Liu, "Multiply charged gas-phase NaAOT reverse micelles: Formation, encapsulation of glycine, and collision-induced dissociation", *Int. J. Mass Spectrom.*, 2010, 293, 12.
2) Y. Fang, A. Bennett, and J. Liu, "Selective transport of amino acids into the gas phase: Driving forces for amino acid solubilization in gas-phase reverse micelles", *Phys. Chem. Chem. Phys.*, 2011, 13, 1466.
3) Y. Fang, F. Liu, and J. Liu, "Mass Spectrometry Study of Negatively Charged, Gas-phase NaAOT Direct Micelles: How Does Charge State Affect Micellar Structure in the Gas Phase?", submitted, 2012

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