Gas-Phase Micellar Assemblies:
Charge-State Dependence of Micellar Structures and Its Applications

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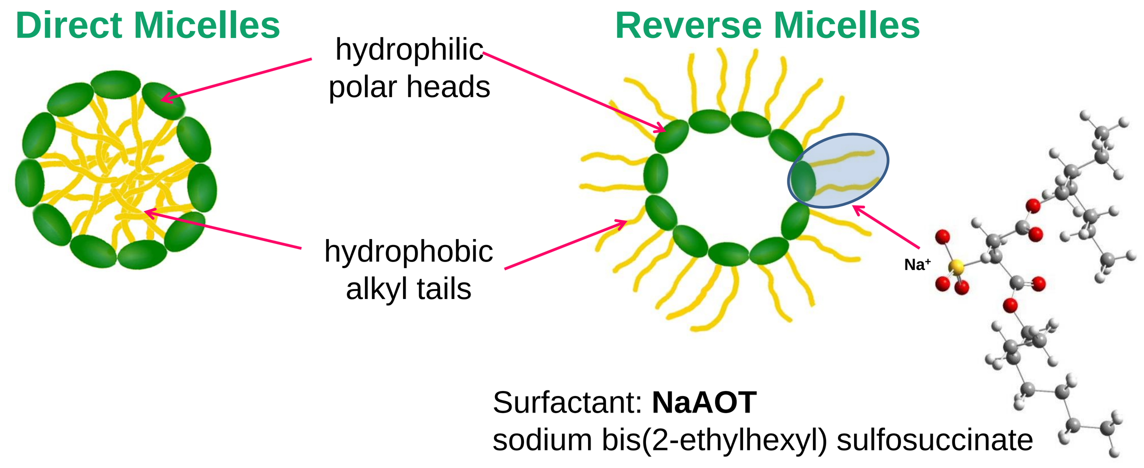
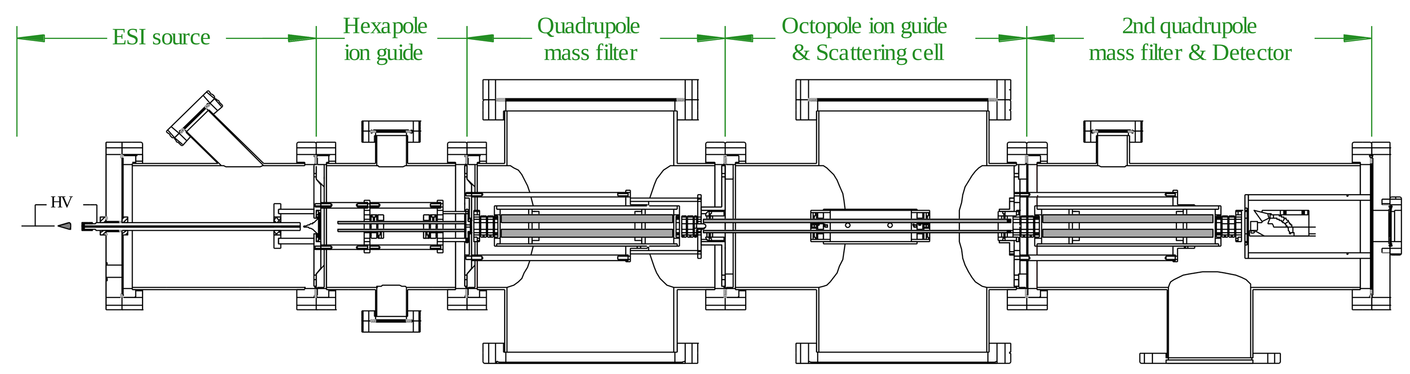
I. Motivation

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

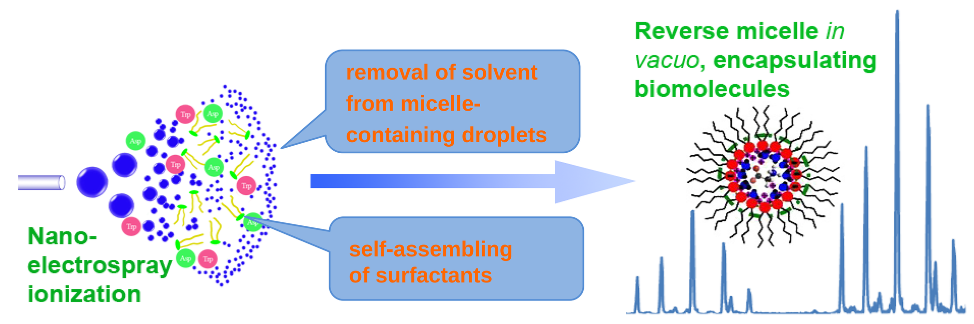


II. Apparatus & Methods

ESI Guided-Ion-Beam Tandem Mass Spectrometer

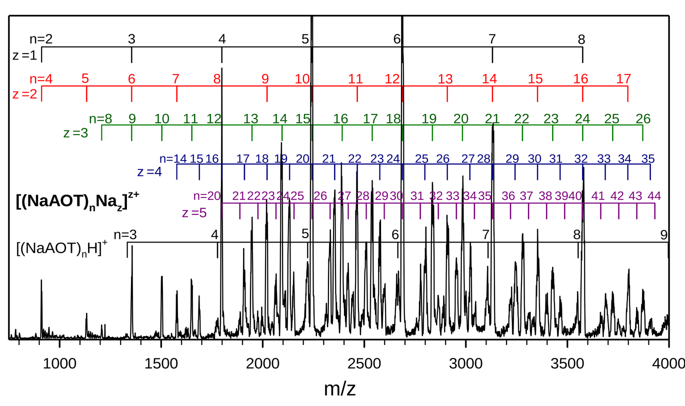


ESI of NaAOT solution, followed by
1) transfer of existing micelles to the gas phase, and
2) self-assembling of surfactants into micellar assemblies in the gas phase



III. Results

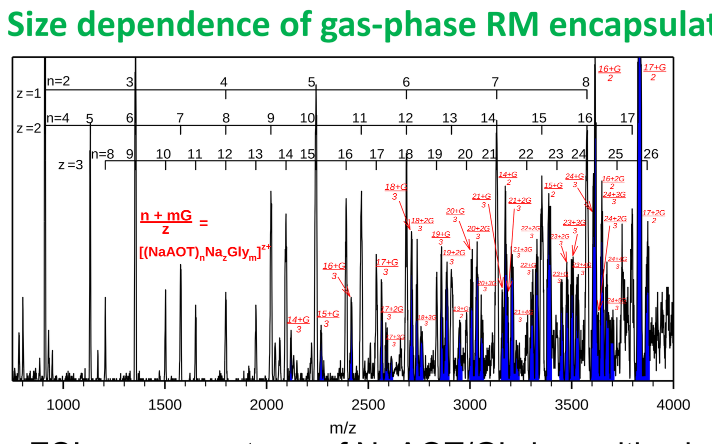
❶ Formation of Multiply Positively-Charged NaAOT Reverse Micelles in The Gas Phase



↑ ESI mass spectrum of NaAOT in positive ion mode

❷ Reverse-Micellar Structure & Encapsulation of Glycine

Size dependence of gas-phase RM encapsulation



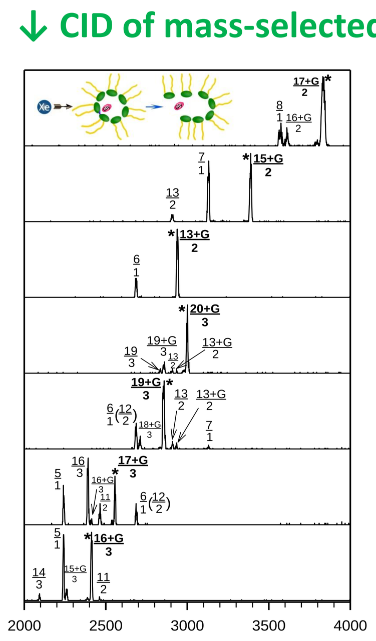
↑ ESI mass spectrum of NaAOT/Gly in positive ion mode

RM aggregation number	Max. number of Gly encapsulated	Core diameter D (nm)
n < 13	0	
n ≥ 13	1	1.4
n ≥ 16	2	1.6
n ≥ 17	3	1.7
n ≥ 21	4	1.9
n ≥ 24	5	2.1

- Core dia. $D = \sqrt{n \times AOT\ polar\ head\ (0.52\ nm^2)/\pi}$
- Size of Gly: 0.6 - 0.7 nm

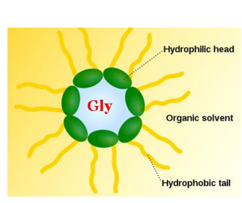
➔ **The max. number of encapsulated Gly correlates with micellar core size.**

↓ **CID of mass-selected Gly-encapsulating micellar ions**

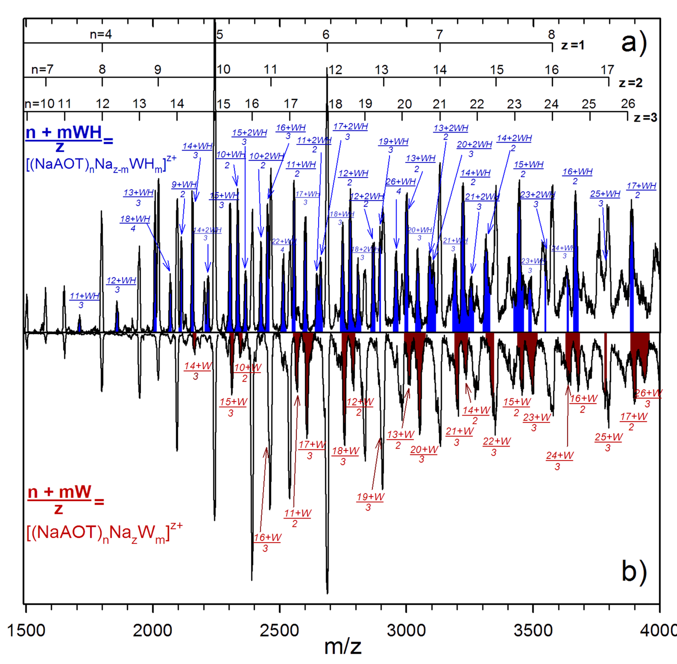


- CID leads to breakdown of micellar aggregates, in order to eject encapsulated Gly

➔ **Gly is confined within the internal core of reverse micelle.**



❸ Driving Forces for Incorporating Hydrophilic *vs.* Hydrophobic Amino Acids



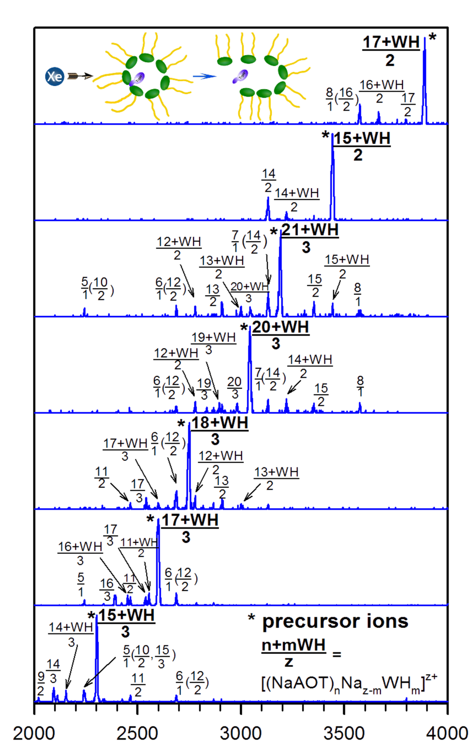
← Positively charged reverse micelles occupied with protonated tryptophan WH^+ (hydrophilic)

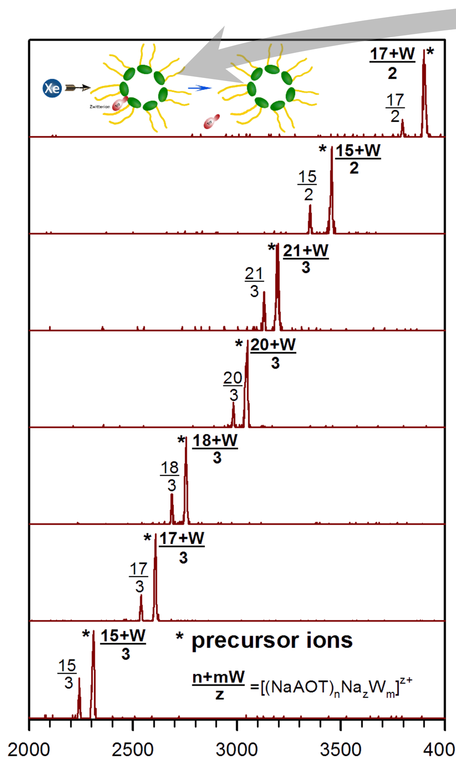
← Positively charged reverse micelles occupied with neutral tryptophan **W** (hydrophobic)

- Encapsulation of WH^+ starts from small size micelles
- Medium to large size micelles each can carry more than one WH^+, but only one **W** at most.

➔ Gas-phase reverse micelles have higher affinity toward protonated tryptophan WH^+

↓ **Use CID to probe site locations of WH^+ and W in reverse micelles**

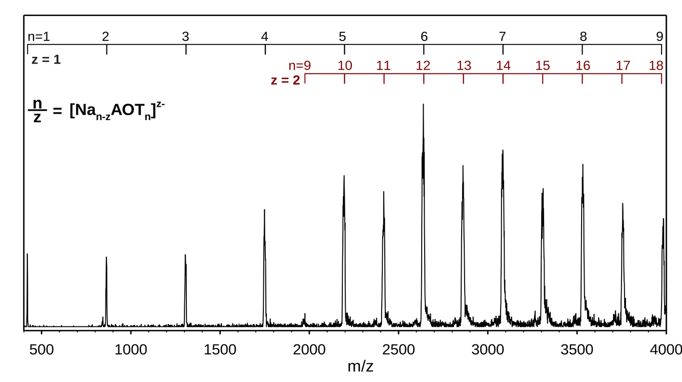




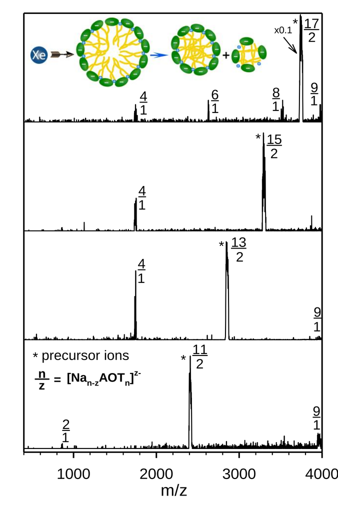
- CID of WH^+ containing reverse micelle leads to breakdown of micellar structure
- CID of **W**-containing reverse micelle lead to stripping only **W** off the micelle

➔ **WH^+ is encapsulated inside micellar core *via electrostatic effects;* W is intercalated between AOTs *via hydrophobic & electrostatic effects.***

❹ *How Does Charge State Affect Micellar Structures & Encapsulation ?*



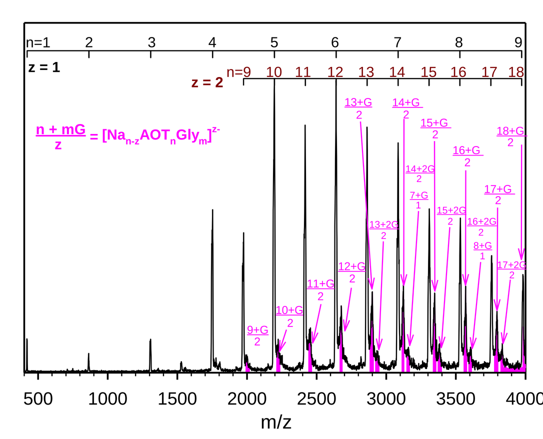
↑ ESI mass spectrum of NaAOT in negative ion mode

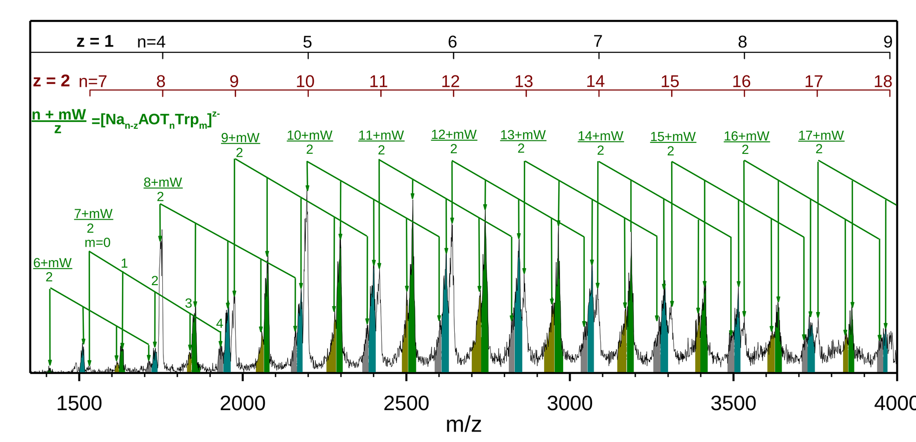


← CID of mass-selected ⊖ charged micelles

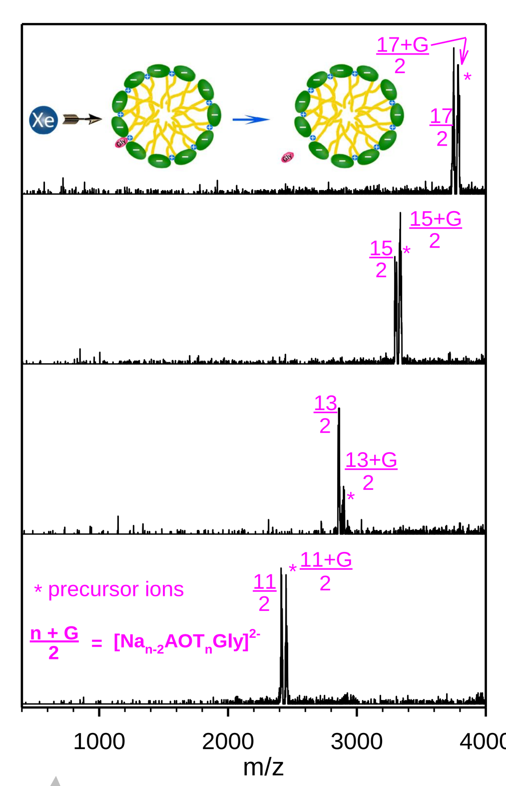
- **Asymmetric Fission**
  Sizes of two fragment ions produced from a ⊖ aggregate differ greatly (*vs.* **Symmetric Fission** of ⊕ charged reverse micelles)

↓ **Encapsulation of hydrophilic Gly *vs.* hydrophobic Trp in ⊖ charged micelles**

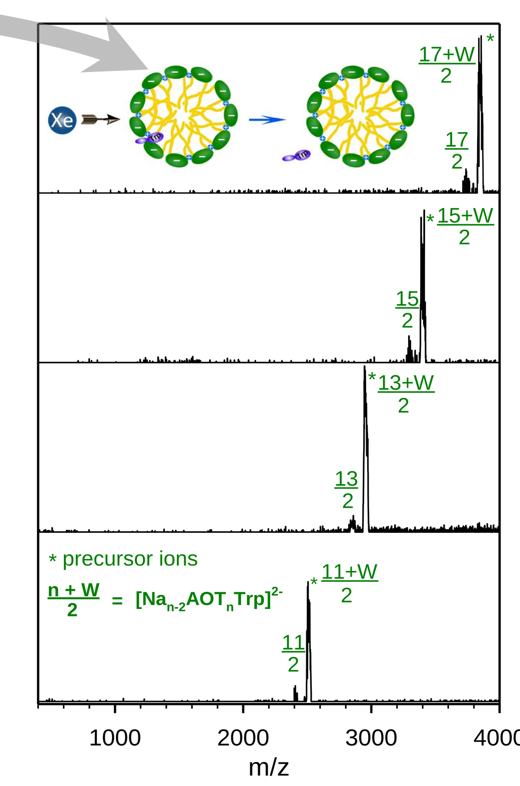




CID of mass-selected ⊖ charged micelles containing Gly (left) or Trp (right)



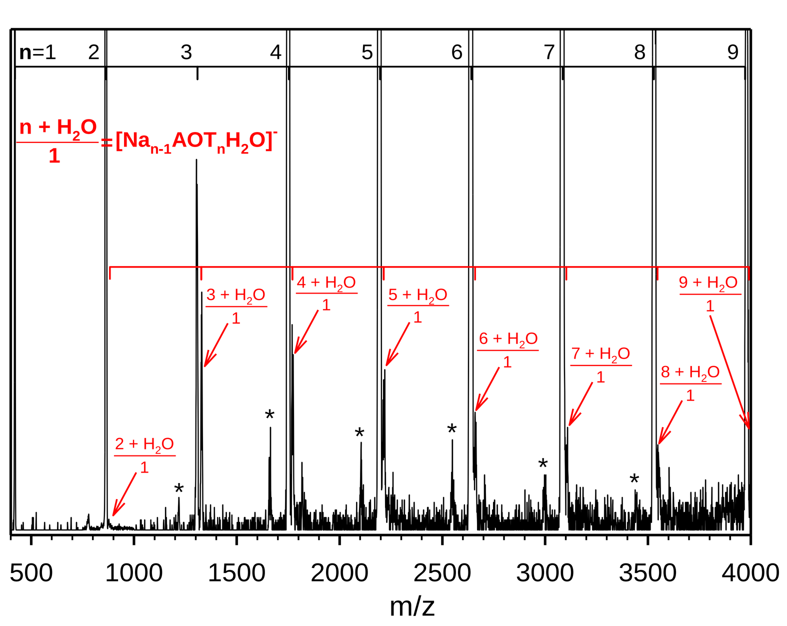
- CID of both Gly- and Trp-containing negatively charged NaAOT micelles lead to stripping only Gly or Trp off micellar aggregates.
- These CID patterns contrast with those of neutral Gly- *vs.* Trp-containing positively charged NaAOT reverse micelles, shown in ❷ and ❸.



- These imply different encapsulation behaviors of ⊕ and ⊖ charged NaAOT micelles, as indicated by cartoons inserted in the figures.

➔ **Direct micelle-like structure for ⊖ charged micellar assembly**

❺ Step towards Generate *Aqueous Solution* in The Gas Phase



↑ ESI mass spectrum of NaAOT/water in negative ion mode

IV. Conclusions

❖**NaAOT surfactants are able to self-assemble into highly-ordered micellar structures in the gas phase.**
❖**Charge state affects 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 reverse and direct micelles.**

Future Directions
❖ **Assembling of "Aqueous Solution" in gas-phase NaAOT micelles**
❖ **Reactions of single biomolecules encapsulation in gas-phase bio-membrane mimetic systems**

1) Y. Fang, F. Liu, and J. Liu, "Mass spectrometry study of negatively charged, gas-phase NaAOT micelles: How does charge state affect micellar structure in the gas phase?", *J. Am. Soc. Mass Spectrom*. 2013, **24**, 9.
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", *PCCP*, 2011, **13**, 1466.
3) 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.

Acknowledgements

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