Formation, Characterization, and Application of Gas-Phase, Multiply Charged Reverse Micelles

Jianbo Liu*, Yigang Fang, William Pineors

Department of Chemistry, Queens College &
The Graduate Center of the City University of New York

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Reverse Micelles (RMs)

One of the most interesting nanometer-sized structures

- selective encapsulation/solubilization
- catalysis
- membrane-mimetic system

NaAOT, sodium bis(2-ethylhexyl) sulfosuccinate, a surfactant molecule commonly used for making RMs
Formation of Gas-Phase RM

**Approach**

**In Nature**
*(marine aerosols)*

1. Formation of aerosol particles at the sea surface
2. Transfer of micelle-contained droplets to the gas phase, evaporation of water
3. RM in the gas-phase, maintaining encapsulated minerals and small organics


**In Laboratory**

Nano-electrospray ionization of micelle solution

Reverse micelle-contained droplets

Transfer to the gas phase, removal of solvent, then exposure to the vacuum

RM in *vacuo*, encapsulating biomolecules

Part I
Formation of Gas-Phase AOT RM & Encapsulation of Gly

ESI solution:
5 mM NaAOT in hexane, \( \omega_0 \) ([water]/[AOT]) = 10

[Similar spectrum was obtained using 5 mM NAOT in methanol/water]

ESI solution:
Same as above, except into which Gly was added ([Gly] = 1 mM)

\[
[(\text{NaAOT})_n\text{Na}_z\text{Gly}_m]^{z+} = \frac{n + mG}{z}
\]
Size Dependence of Gas-Phase RM Encapsulation

<table>
<thead>
<tr>
<th>Aggregation number $n$</th>
<th>Core diameter (nm)</th>
<th>Max. number of Gly encapsulated in RM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n &lt; 13$</td>
<td>—</td>
<td>0</td>
</tr>
<tr>
<td>$n \geq 13$</td>
<td>1.4</td>
<td>1</td>
</tr>
<tr>
<td>$n \geq 16$</td>
<td>1.6</td>
<td>2</td>
</tr>
<tr>
<td>$n \geq 17$</td>
<td>1.7</td>
<td>3</td>
</tr>
<tr>
<td>$n \geq 21$</td>
<td>1.9</td>
<td>4</td>
</tr>
<tr>
<td>$n \geq 24$</td>
<td>2.1</td>
<td>5</td>
</tr>
</tbody>
</table>

Core diameter: \[ D = \sqrt{n \times A / \pi} \]

A is the area of the AOT polar head (0.52 nm$^2$)

Size of Gly: 0.6-0.7 nm
Collision-Induced Dissociation (CID) Cross Section As a Function of $E_{\text{col}}$

Empty gas-phase RM

Gas-phase RM encapsulating Gly

Collision-Induced Dissociation (CID)
Cross Section As a Function of $E_{\text{col}}$

\[ \sigma_{\text{HS}} = \pi \cdot (r_1 + r_2)^2 \]

At highest $E_{\text{col}}$, $\sigma_{\text{cid}}$ is approaching the hard-sphere collision limit.

Another piece of evidence that gas-phase AOT forms spherical reverse micellar structure.
Part II

Driving Forces for Solubilization:

Electrostatic vs. Hydrophobic

In Solution-Phase RM

Hydrophilic biomolecule (e.g. Gly, TrpH+) located in the internal core — electrostatic interaction

Hydrophobic biomolecule (e.g. neutral Trp) located at the interface — hydrophobic interaction

Driving Force for Solubilization in Gas-Phase RM?

Top:
RM occupied with protonated TrpH⁺

Bottom:
RM occupied with neutral Trp (hydrophobic)
Probing Guest Molecule Location Using CID: 
Encapsulation Inside vs. Attached to the Interface

WH = TrpH*, protonated Trp

W = Trp, neutral Trp
Part III

Selectivity Between Two AAs
Case (1): Aspartic Acid vs. Tryptophan

ESI of AOT/Asp

\[
\frac{n + mDH}{z} = \frac{([NaAOT]_n Na_{z-m} AspH_m)^{z+}}{nn+ DH}
\]

ESI of AOT/Asp+Trp

\[
\frac{n + mWH}{z} = \frac{([NaAOT]_n Na_{z-m} TrpH_m)^{z+}}{nn+ WH}
\]

m/z

1500 2000 2500 3000 3500 4000
Case (2): Arginine vs. Tryptophan

No changes when mixed with Trp!
Only Arg detected,
no encapsulation of Trp
Fundamentals of Selectivity

<table>
<thead>
<tr>
<th></th>
<th>Aspartic acid (D)</th>
<th>Tryptophan (W)</th>
<th>Proline (P)</th>
<th>Arginine (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK_a$ of $\alpha$-COOH</td>
<td>1.9</td>
<td>2.8</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>$pK_a$ of $\alpha$-NH$_3^+$</td>
<td>9.6</td>
<td>9.4</td>
<td>10.6</td>
<td>9.0</td>
</tr>
<tr>
<td>$pK_a$ of acidic R</td>
<td>3.7</td>
<td>-</td>
<td>-</td>
<td>12.5</td>
</tr>
<tr>
<td>$pI$</td>
<td>2.8</td>
<td>5.9</td>
<td>6.3</td>
<td>10.8</td>
</tr>
</tbody>
</table>

$pH$ of ESI solution of AOT/(Trp + Asp) in methanol/water = 5.1

$pH$ of ESI solution of AOT/(Trp + Arg) in methanol/water = 7.4

**Selectivity between different AAs?**

- Selectivity reflects a competition between electrostatic and hydrophobic forces, which can be tuned up by changing the pH of ESI solution.
- Amino acid with a higher $pI$ exists in protonated form and has a larger affinity with AOT$^-$ (i.e. Arg > Trp > Asp)
Conclusions

- NaAOT surfactants are able to form RM in the gas phase.

- Gas-phase RM can act as nanometer-sized vehicle for selective transport of non-volatile biomolecules into the gas phase.

- Driving force for solubilization: electrostatic & hydrophobic interactions.

**Application in Analytical Chemistry:**

*Separation and Direct Determination* of ionic and neutral amino acids in solution.
Acknowledgements

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