# Gas Phase Infrared Multiple Photon Dissociation Spectra of Positively Charged Sodium Bis(2-ethylhexyl)sulfosuccinate Reverse Micelle-like **Aggregates**

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ABSTRACT: The capability of infrared multiple photon dissociation (IRMPD) spectroscopy to gain structural information on surfactant-based supramolecular aggregates has been exploited to elucidate intermolecular interactions and local organization of positively charged sodium bis(2-ethylhexyl)sulfosuccinate (AOTNa) aggregates in the gas phase. A detailed analysis of the stretching modes of the AOTNa CO and  $SO_3^{-}$  head groups allows one to directly probe their interactions with sodium counterions and to gain insight in their organization within the aggregate. Similarities and differences of the IRMPD spectra as compared to the infrared absorption spectrum of micellized AOTNa in CCl<sub>4</sub> have been analyzed. They strongly suggest a reverse micellelike organization of AOTNa charged aggregates in the gas phase. Apart from low-abundance fragmentation channels of the AOTNa (molecule) itself, the



main dissociation pathway of singly charged surfactant aggregates is the loss of neutral surfactant molecules, while doubly charged aggregates dissociate preferentially by charge separation forming singly charged species. In both cases, decomposition leads to the formation of the most energetically stable charged fragments.

# INTRODUCTION

Sodium bis(2-ethylhexyl)sulfosuccinate (AOTNa, Scheme 1) is a well-known dichained anionic surfactant widely employed to form reverse micelles in apolar media.<sup>1</sup>

Mainly driven by favorable interactions between sodium counterions and sulfosuccinate heads of the surfactant molecules, these nearly spherical aggregates are characterized by an internal core consisting of polar moieties surrounded by an apolar layer formed by the surfactant alkyl chains.<sup>2</sup>

AOTNa can also be dissolved in water where, above the critical micellar concentration, it forms direct micelles.<sup>3</sup> Under such conditions, as a consequence of hydrophobic interactions, AOT-Na molecules are oriented within the aggregate so that the alkyl chains form the internal core, while hydrated sodium counterions and surfactant heads constitute the external layer.<sup>4</sup>

Charged AOTNa aggregates were first observed in mass spectra using fast atom bombardment (FAB) as an ionization technique by Lyon et al.<sup>5</sup> More recently, by using electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) mass spectrometry, it has been observed that AOTNa self-assembles in the gas phase forming species with an aggregation number up to 22. $^{6-11}$ 

While there is no doubt that in gas phase AOTNa forms reverse micelle-like aggregates,<sup>12</sup> the absence of additional interactions due to the surrounding solvent molecules and the presence of one or more extra charges in the aggregate could induce structural alterations, which are of interest for both theoretical and technological reasons.

Here we provide direct experimental evidence of the structural organization of charged surfactant aggregates in gas phase by applying infrared multiple photon dissociation (IRMPD) spectroscopy.<sup>13</sup> This technique is based on the fragmentation of mass-selected ionic species induced by a tunable monochromatic infrared laser radiation. Due to the strong coupling among intramolecular motions, in fact, the multiple excitation of a specific vibrational mode is rapidly transferred to the other internal motions until the total energy of the species is enough to access one or more fragmentation channels.<sup> $t_4$ </sup> Only very few applications of IRMPD<sup>15-17</sup> to noncovalently self-assembled

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systems have been published, but none of them concerns either micellar aggregates or surfactant.

Here we show that, through the possibility of collecting the fragmentation yield of mass-selected ionic species as a function of the frequency of the infrared laser, detailed knowledge of the intermolecular interactions within positively charged AOTNa aggregates can be obtained. A further interesting potential of IRMPD spectroscopy is to investigate whether, in the case of noncovalently organized supramolecular aggregates, the selective excitation of different vibrational modes could affect differently the fragmentation yield and/or the various decomposition channels.

#### EXPERIMENTAL SECTION

**Materials.** AOTNa (99%) was purchased from Sigma-Aldrich-Fluka (Milan, Italy). Solutions were prepared using water, methanol and *n*-hexane of spectroscopic grade.

**IRMPD.** IRMPD spectra were recorded at the FELIX facility (FOM Rijnhuizen, Netherlands). The experimental apparatus consists of a Fourier transform ion cyclotron mass spectrometer equipped with an electrospray ion source (Micromass Z-spray). A  $2.7 \times 10^{-3}$  M solution of AOTNa in water/methanol (50/ 50% vol) has been introduced via direct infusion at a flow rate of 10  $\mu$ L/min.

In particular, at each wavenumber ( $\nu$ ) of the exciting infrared laser radiation, three mass spectra are acquired, and the averaged integrated intensities of the parent ion ( $I_p(\nu)$ ) and of its fragments ( $I_{f,i}(\nu)$ ) are employed to calculate the fragmentation degree  $Y(\nu)$  according to eq 1:

$$Y(\nu) = \frac{\sum_{i} I_{f_{i}i}(\nu)}{I_{p}(\nu) + \sum_{i} I_{f_{i}i}(\nu)}$$
(1)

The high pulse energies (about 50 mJ per 5  $\mu$ s pulse in these experiments) in a wide frequency range, and the narrow bandwidth (about 0.5% of the central wavelength) of FELIX makes it an ideal tool to probe the structure of supramolecular aggregates in gas phase by IRMPD spectroscopy.<sup>18</sup>

Fourier Transform Infrared (FT-IR) Spectroscopy. FT-IR spectra of a reverse micelle solution of 0.1 M AOTNa in  $CCl_4$  were acquired at 25 °C with a Spectrum One FT-IR spectrometer (Perkin-Elmer, Shelton (USA)), using a cell equipped with  $CaF_2$  windows. Each IR spectrum was the average of eight scans in the

 $900-4000 \text{ cm}^{-1}$  wavenumber range at a spectral resolution of 0.5 cm<sup>-1</sup>.

#### RESULTS AND DISCUSSION

Fragmentation Pattern of Singly and Doubly Charged AOTNa Aggregates. The multiple photon excitation of the  $[AOTNa_2]^+$  ion leads, as main fragments, to the  $[AOTNa_2^- C_8H_{16}]^+$  (m/z 355) and  $[HO-CO-CH_2-CH_2-SO_3Na_2]^+$  (m/z 199) species, corresponding to the loss of one or both surfactant alkyl chains. On the other hand, the photodissociation of higher-order singly charged AOTNa aggregates is dominated by the loss of individual surfactant molecules, caused by the much lower energy barrier for such a process as compared to that required for the cleavage of a C–O bond. These findings are consistent with the fragmentation patterns observed in collision-induced dissociation as well as with the trend of the collision energy required for 50% dissociation of the ionic species.<sup>9</sup>

As to the doubly charged AOTNa aggregates, the smallest species observed here is  $[AOT_3Na_5]^{2+}$ . For these doubly charged ions, the main fragmentation channel consists of charge separation with the formation of two singly charged aggregates.  $[AOT_3Na_5]^{2+}$  dissociates giving [AOTNa<sub>2</sub>] plus  $[AOT_2Na_3]^+$  in nearly the same abundance.  $[AOT_5Na_7]^{2+}$ and  $[AOT_7Na_9]^{2+}$  dissociate giving, in order of decreasing abundance,  $[AOT_3Na_5]^{2+}$ ,  $[AOTNa_2]^+$  and  $[AOT_2Na_3]^+$ . It is worth noting that the decomposition of singly and doubly charged aggregates seems to reflect the relative stability of charged fragments and that, in the case of the coexistence of various fragmentation channels, the different vibrational modes couple similarly. This implies that the energy transfer among the vibrational degrees of freedom of the organized AOTNa aggregates is fast and efficient. This finding is consistent with the picture of gas-phase reverse micelle-like aggregates whose center is occupied by the sodium counterions and SO<sub>3</sub><sup>-</sup> surfactant head groups interacting through strong Coulomb interactions and forming a very compact solid-like aggregate core.<sup>12</sup>

IRMPD Spectra of Singly and Doubly Positively Charged AOTNa Aggregates. The IRMPD spectra of gas-phase singly and doubly positively charged AOTNa aggregate ions in the wavenumber range from 900 to  $1800 \text{ cm}^{-1}$  obtained by infusion of an AOTNa solution in water/methanol are shown in Figures 1 and 2, respectively. For comparison, the IR spectrum of AOTNa reverse micelles in CCl<sub>4</sub> is also reported.

According to literature, all the bands shown in Figure 1 can be attributed to the functional groups of AOTNa.<sup>19,20</sup> The assignments of the main observed frequencies are summarized in Table 1. The most significant, which will be analyzed here in detail, are the bands due to the stretching modes of the CO and  $SO_3^-$  groups.

Apart from a scale factor, it is interesting to note the close resemblance of gas-phase IRMPD spectra with that in condensed apolar phase obtained by traditional absorption spectroscopy. The major difference is the much higher intensity of the IRMPD bands occurring at about 1300 and 1400 cm<sup>-1</sup>, attributable to methylene twisting and bending modes, with respect to IR bands in the apolar phase. This is possibly due to some saturation occurring on the stronger bands in the IRMPD spectrum, which makes the weaker bands appear with a relatively higher intensity. However, new bands or an increased intensity of weak bands may



**Figure 1.** IRMPD spectra of AOTNa singly positively charged ions and IR spectrum of 0.1 M AOTNa in carbon tetrachloride (dashed lines are a guide for the eye).



**Figure 2.** IRMPD spectra of AOTNa doubly positively charged aggregates and IR spectrum of 0.1 M AOTNa in carbon tetrachloride (dashed lines are a guide for the eye).

also be induced by the ionic nature of the gas-phase aggregates versus their neutral state in solution.

Spectral trends appearing as a function of the aggregation number (N) and charge state of AOTNa aggregate ions can be observed, indicating that IRMPD spectra are a sensitive probe of the surfactant organization in the aggregate.

**CO Stretching Band.** In the condensed phase, AOTNa reverse micelles show a CO stretching band centered at 1737  $\text{cm}^{-1}$  with a shoulder at 1720  $\text{cm}^{-1}$ , which have been assigned to

gauche and anti conformations about the acyl C–C bond of the succinate moiety, respectively.<sup>21,22</sup> On the other hand, a perusal of Figures 1 and 2 shows that the band due to the CO stretching of AOTNa charged aggregates in the gas phase is red-shifted with respect to that observed in the condensed phase. This suggests that, in absence of apolar solvent and/or in the presence of an extra charge, the interaction between the sodium counterions and the carbonyl groups is stronger, withdrawing more electron density from the C=O bond shifting its frequency to the red.<sup>17</sup> Moreover, the symmetric and relatively narrow shape of the CO stretching band suggests that the structural arrangement of AOTNa molecules in the gas phase aggregates should be such that the environment probed by these groups is similar.

A closer look at the CO band position ( $\nu$ (CO)) for both singly and doubly charged ions as a function of N is shown in Figure 3. It is of interest to note that the CO band position of  $[AOTNa_2]^+$ , occurring at 1704 cm<sup>-1</sup>, is very close to that (1706–1708 cm<sup>-1</sup>) which has been assigned to the surfactant CO group coordinated with the Na<sup>+</sup> counterion in the condensed phase.<sup>23</sup> It can be also seen that, after an initial increase in frequency, indicating a progressive weakening of the  $CO \cdots Na^+$  interaction with N, the band position tends to a plateau, never reaching the condensed-phase value in CCl<sub>4</sub>. While this may be due to differences between AOTNa self-assembling in the gas phase and in apolar solution, the small shift may also be induced by the presence of the additional charge in the gas-phase clusters. This appears to be supported by the observation that the CO stretch of doubly charged aggregates shows an additional red shift with respect to that of singly charged ones with the same aggregation number.

This feature shows that, in addition to the effect due to the number of AOTNa molecules forming the aggregate, a significant contribution to the CO band position is given by the presence of additional sodium counterion(s). The observed behavior suggests that the AOTNa molecules are arranged in ordered aggregates in which the CO groups interact with the sodium counterions within the aggregate core and the lipophilic chains are oriented outward.

**1130–1330** cm<sup>-1</sup> **Band.** A broad band is observed in the 1130–1330 cm<sup>-1</sup> region (Figures 1 and 2), which mainly constitutes the vibrational modes of the  $SO_3^-$  antisymmetric stretching vibrations (about 1216 and 1250 cm<sup>-1</sup>), those due to the C–O and C–C stretching bands of the ester linkage (main contribution appearing as a shoulder at about 1160 cm<sup>-1</sup>), and those due to CH<sub>2</sub> twisting modes.<sup>20</sup> Since this band originates from contributions arising from different groups, its analysis is more intricate. In addition, the environment probed by the  $SO_3^-$  is better reflected in the symmetric stretching band near 1050 cm<sup>-1</sup> (see below). To avoid redundant argumentations, we refrain from a further analysis of the 1130–1330 cm<sup>-1</sup> spectral region.

**SO**<sub>3</sub><sup>-</sup> **Symmetric Stretching Band.** The position of the surfactant SO<sub>3</sub><sup>-</sup> symmetric stretching band for both singly and doubly charged ions, occurring at about 1050 cm<sup>-1</sup>, as a function of *N* is shown in Figure 4. At first glance, it can be observed that the SO<sub>3</sub><sup>-</sup> group is also sensitive to the structural evolution of gasphase AOTNa aggregates as a function of *N* and to the charge state. In particular, it can be noted that the band is progressively blue-shifted with increasing *N*, reaching a plateau at higher values. This blue shift, as well as that induced by an increase of the charge state of the aggregate, results from the increase of the number and strength of the sulfonate-sodium counterion interactions with *N* and with the number of extra sodium ions.<sup>20</sup>

wavenumber $(cm^{-1})$		
AOTNa charged aggregates	AOTNa/CCl <sub>4</sub>	group assignments
1704-1725	1737	ν(CO)
1463-1465	1464	$\delta_{ m as}( m CH_3)+ m CH_2$ sciss
1390-1395	1393	$\delta(CH_2)$
1130-1350	1130-1310	$\nu_{as}(SO_3^-) + \nu(C-C(O)-O)$ , CH <sub>2</sub> twist
1042-1056	1052	$\nu_{s}(\mathrm{SO}_{3}^{-})$

Table 1. Infrared Frequencies and Assignments of AOTNa in Gas-Phase Charged Aggregates and as Reverse Micelles Dispersed in CCl<sub>4</sub>



**Figure 3.** CO stretching band position as a function of the aggregation number (N) ( $\blacksquare$  singly charged,  $\bullet$  doubly charged aggregates. Dashed line, value in CCl<sub>4</sub> solution).



**Figure 4.**  $SO_3^-$  band position as a function of the aggregation number (N) ( $\blacksquare$  singly charged,  $\bullet$  doubly charged aggregates. Dashed line, value in CCl<sub>4</sub> solution).

On the other hand, the mismatch of the plateau value with the band position in apolar phase suggests that some differences should exist between AOTNa self-assembling in the gas phase and in apolar solution.

Apart from the IRMPD spectra of the  $[AOTNa_2]^+$  and  $[AOT_2Na_3]^+$  species, it can be also noted that the main peak

at about 1050 cm<sup>-1</sup> is accompanied by a smaller peak at about 1009 cm<sup>-1</sup>. The presence of the latter has been attributed to the nonequivalent environments of the oxygen atoms of the  $SO_3^-$  group.<sup>24</sup> Therefore, the absence of this peak in the  $[AOTNa_2]^+$  spectrum suggests that in this case the three oxygen atoms of the  $SO_3^-$  group are practically equivalent, whereas the  $[AOT_2Na_3]^+$  spectrum seems to indicate some specific arrangement of sodium counterions and  $SO_3^-$  groups dictated by the symmetry of the aggregate.

# CONCLUSION

This work has shown that IRMPD spectroscopy can be usefully applied in the study of surfactants, and it gives information on the structure and local organization of their supramolecular aggregates. In particular, information on structural features of singly and doubly charged AOTNa aggregates in the gas phase has been obtained.

The analysis of the IRMPD spectra suggests that the gas phase aggregates are reverse micelle-like entities where sodium counterions and surfactant head groups closely interact in the aggregate core surrounded by the surfactant alkyl chains. Spectral differences with aggregates in apolar phase are suggested to be due to the presence of the extra charge and the absence of surrounding solvent molecules.

IRMPD data have also been useful to shed some light on the fragmentation patterns and yields induced by infrared multiphoton irradiation of supramolecular surfactant-based charged aggregates. Despite the low IR absorption coefficient, the photoexcitation of methylene bending mode induces clearly observable fragmentation of the AOTNa aggregates. While singly charged aggregates preferentially lose neutral surfactant molecules, doubly charged aggregates dissociate by charge separation into singly charged species.

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