

Electrospray ionization mass spectrometry of surfactant - metal ions attachment: Sensitivity and in-source fragmentation

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Abstract—Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICR-MS) is used to investigate the reaction of non-ionic ethylene oxide based surfactants, with divalent metal ions. The effect of capillary-skimmer potential difference and the ion residence time in the hexapole ion trap in the external ion optic of the FT mass spectrometer were systematically investigated for the single oligomer systems, hexaethylene glycol monodecyl ether (HEGMDE) interacting with the nitrate salts of Cd(II) in methanol. It is observed that these variables impact significantly on the type of ions observed in the ESI experiment and hence the mass spectra and so it is essential to identify their contribution prior to undertaking any binding efficiency experiments. Collision induced dissociation in the capillary skimmer region and by on resonance irradiation is used to investigate structures and fragmentation pathways. In particular the loss of HNO₃ in the nitrate salts is a favoured reaction pathway for compounds with acidic protons.

Keywords: surfactants, heavy metals, mass spectrometry, collision induced dissociation, environment.

I. INTRODUCTION

Polymer surfactants are widely used in industry to extract heavy metals from contaminated water supplies and so it is of interest to study the chemistry and chemical bonding involved in these purification procedures¹⁻⁵. Collision induced dissociation is a powerful tool that provides useful information on structure, fragmentation pathways, and the thermodynamic behavior of gas ions. Several different techniques have been developed for ion structure determination, but CID remains one of the most useful and widely implemented mass spectrometric techniques, especially when employed in tandem techniques for complex mixture analysis.⁶⁻⁷

Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry is a powerful technique that shows promise for rapid screening of binding selectivities in host-guest chemistry⁸⁻¹⁴. We have used high-resolution ESI-FTICR-MS to evaluate the relative efficiencies of attachment and chemical bonding of selected transition metal cations and metal cation adducts (where the adducts are negative-ions) to non-ionic surfactants and hydrophilic polymers. The purpose of using CID to confirm the loss of HNO₃ from [TEG+ZnNO₃]⁺. Experimental variables which appear to have an effect on the attachment of the metal-ions

to the surfactants and polymers including the capillary-skimmer voltages in the ESI source (Important for collision-induced-dissociation processes), the external ion source ion optics voltages as well as the ion-trapping times in the hexapole ion storage trap and the ICR cell have been studied. All the CID experiments described in work is performed with on-resonance irradiation (ORI).

II. EXPERIMENTAL

The metal complexes were produced by mixing solutions of the nitrate salt of Cd(II) with the surfactant (HEGMDE) in methanol (HPLC grade). The mole ratio is 1:1 for the HEGMDE-Cd(II) salt mixture and the concentration of each component before mixing is 1.5×10^{-4} M. A Bruker BioApex-II 7T FTICR mass spectrometer with an on- and off-axis Analytica ESI spray source was used in this study. (Schematic 1). Stronger signals were observed using the off-axis configuration. Data acquisition (512K spectra) and processing were performed using Xmass-6.2 on a PC.

In this work we studied Cd(II) guest cations with the following host surfactant:



Hexaethylene glycol monodecyl ether

III. RESULTS AND DISCUSSIONS

The interaction of HEGMDE with selected divalent metal ions, as studied by ESI-FTICR mass spectrometry, indicate that complexes were formed between HEGMDE and Cd(NO₃)₂, and all form HEGMDE complexes with the stoichiometric HEGMDE : metal of 3:1. The relative intensities of the HEGMDE/ Cd(II) complexes that were detected and optimized by ESI-FTICR mass spectrometry are shown in Figure 1. The complexes are assigned to peaks at m/z 598.214315, 690.437635, 901.602438, and 1020.541783 corresponding to the ions

$[\text{HEGMDE}+\text{CdNO}_3]^+$, $[(\text{HEGMDE})_3+\text{Cd}]^{2+}$, $[(\text{HEGMDE})_4+\text{Cd}]^{2+}$, and $[(\text{HEGMDE})_2+\text{CdNO}_3]^+$ respectively. All of these clusters were observed at CSPD 10V. By increasing CSPD to 300 V clusters fragmented to form $[\text{HEGMDE}+\text{Cd}-\text{H}]^+$. It is proposed that Cd(II) reacts with HEGMDE through the 6-mers of internal chains of ethylene oxide. Cd(II) can coordinate to seven oxygen atoms in a planer fashion and also coordinate to two other atoms above the plane which adopts a more bent conformation.

The minimized structure estimated by a molecular mechanics (MM2) program (chem3D ver.9.0; CambridgeSoft) indicates that 6-mers in the HEGMDE molecule have similar features as a crown ether. The HEGMDE chain encircles the divalent metal ion [Cd(II)] using seven oxygen sites to support divalent metal cationization and HEGMDE maintains a planer structure with the M(II) ion, while Cd(II) resides above the plane of HEGMDE (Figure 2b). The alkyl groups in HEGMDE do not show any interaction with the Cd(II). The preferred structure, with the Cd(II) ion sitting above HEGMDE plane also show two or more HEGMDE molecules can coordinate to Cd(II), as seen in the mass spectra at low CSPD (Figure 1).

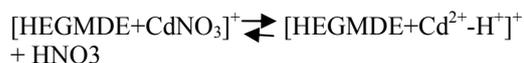
The complex $[\text{HEGMDE}+\text{Cd}-\text{H}]^+$ was used for the MM2 calculations. Figures 2 show the lowest energy structures (side view and top view) found for HEGMDE/Cd(II). Carbon atoms are gray, oxygens are red, and the Co(II) ion is blue. Hydrogens have been omitted. Cd(II) is centered in or slightly above the binding circle and is equidistant from the oxygen atoms of HEGMDE. The ability of the HEGMDE to provide more than five

sites of coordination makes the interaction between HEGMDE and Cd(II) more favorable. Bowers et al. reported that a Na^+ ion can coordinate to 8 oxygen atoms from a PEG molecule in order to form a stable coordination sphere. Due to its large ionic radius, a Cs^+ ion co-ordinates to 11 oxygen atoms from a PEG molecule in order to form a complete stable co-ordination sphere.¹⁵ In another study, the same author found an almost linear increase in the collisional cross-section area of singly sodiated PEG with oligomers size.¹⁶ It is deduced that as the size of the metal ion increases the number of ethylene oxide donor atoms must increase to form a stable complex.

The Effect of Experimental parameters on the attachment of Cd(II) to HEGMDE.

The voltages applied to the capillary/skimmer (C/S) ion optics as well as the trap time in the hexapole ion trap are observed to have a dramatic affect on peaks assigned to the HEGMDE/ Cd(II) complexes observed in the ESI-FTICR positive-ion and negative-ion mass spectra. For example, Figure 3(a) shows that at low C/S voltage-differences (~30V) the complex ion $[\text{HEGMDE}+\text{CdNO}_3]^+$ is observed. At high C/S voltage differences HNO_3 is lost from this ion to form the ion $[\text{HEGMDE}+\text{Cd}-\text{H}]^+$. To confirm that this last process is a CID reaction, an on-resonance CID experiment with argon gas (see Figure 4) was performed on the former cation which subsequently dissociated losing

HNO_3 to produce $[\text{HEGMDE}+\text{Cd}-\text{H}]^+$. The peak corresponding to $[\text{HEGMDE}+\text{ZnNO}_3]^+$ is isolated by a series sweeps and bursts. The isolated complex ion is then excited by an on-resonance rf pulse, resulting in the fragmentation shown in Figure (4) which shows the ORCID positive-ion ESI-FTICR mass spectrum of the complex ion $[\text{HEGMDE}+\text{Cd}^{2+}-\text{H}]^+$.



Furthermore, at low C/S voltage differences (Figure 1) shows peaks that can be assigned to the metalated HEGMDE-clusters $[(\text{HEGMDE})_y+\text{Cd}(\text{II})]^{2+}$, $y=2,3,4$ and $[\text{HEGMDE} +\text{Cd}(\text{II})\text{X}]^+$ $x= \text{NO}_3^-$. Similarly controlled variation of the ion trap-time in the hexapole ion trap is observed to have a dramatic affect on peaks assigned to the host-guest ions observed in the ESI-FTICR mass spectra.

For example, Figure 3(b) shows that at low ion trap-times the host-guest ion $[\text{HEGMDE}+\text{CdNO}_3]^+$ is observed. At high trap-times HNO_3 is lost from this ion to form $[\text{HEGMDE}+\text{Cd}^{2+}-\text{H}]^+$. Due to the similarity of this result with that observed in the C/S CID experiment (Figure 3a) we assume that at increased ion trap-times in the hexapole ion guide the host/guest ions are involved in CID processes.

In general, the amounts of the host/guest ions; $[\text{Oligomer}+\text{Cd}^{2+}-\text{H}]^+$ and $[(\text{Oligomer})+\text{Cd}(\text{II})]^{2+}$ observed in the FTICR mass spectra can be systematically optimized in a controlled way by careful variation of the C/S voltage-difference or the ion trap time in the hexapole ion accumulation trap. Such CID processes are well known in FTICR mass spectrometry but little attention in the literature has been paid to this process and its impact on host-guest chemistry studied by mass spectrometry. Similar results to those above have been observed in this present study for all the surfactants and for the metals cations Co^{2+} and Zn^{2+} .

IV. CONCLUSION

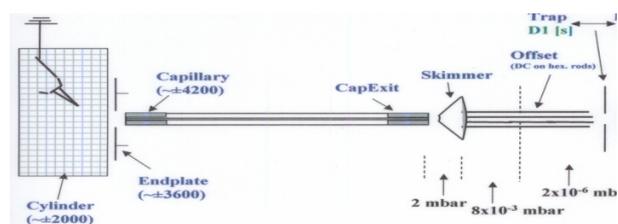
ESI-FTICR-mass spectrometry shows that reaction of the divalent metal ions $M = \text{Cd}^{2+}$ with the surfactants form host/guest ions $[\text{HEGMDE}+\text{MNO}_3]^+$, $[\text{HEGMDE}+\text{M}^{2+}-\text{H}]^+$ and host/guest cluster ions $[(\text{HEGMDE})_n+\text{M}^{2+}]^{2+}$. Future studies will examine the affect of the metal counter ion on the host/guest chemistry. The intensity of the host/guest fragment ion $[\text{oligomer}+\text{Cd}^{2+}-\text{H}]^+$ varies as a function of the capillary-skimmer voltage difference as well as ion-trapping time in the hexapole and its production is enhanced by collisions. Capillary/Skimmer and on-resonance collision induced dissociation experiments confirm that the host/guest ion $[\text{HEGMDE}+\text{CdNO}_3]^+$ fragments to $[\text{HEGMDE}+\text{Cd}^{2+}-\text{H}]^+$. The cluster ions $[(\text{HEGMDE})_n+\text{M}^{2+}]^{2+}$ (where $M = \text{Cd}^{2+}$, $n = 2-4$) are observed only in CID free conditions. For competitive host-guest kinetics, this study shows that it is important to optimize experimental variables that do not artificially bias the results because of tandem processes such as CID.

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Schematic 1. Electrospray ionization source on the FTICR-Mass Spectrometer

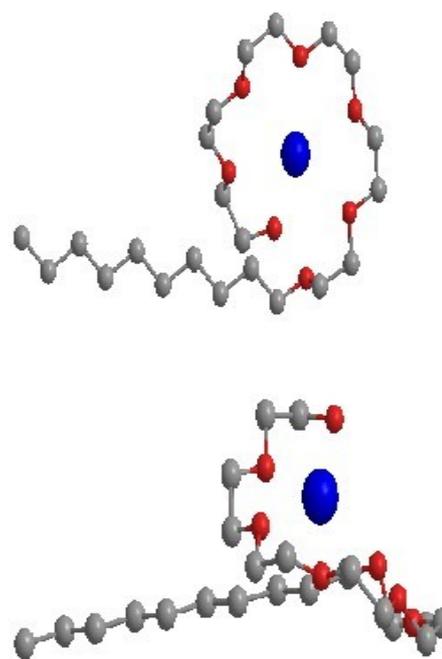
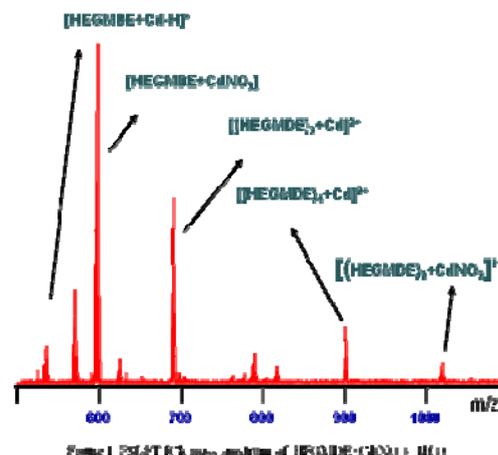


Figure 2 (2a, 2b). Lowest energy conformation of TEG/CoII/Cd(II)

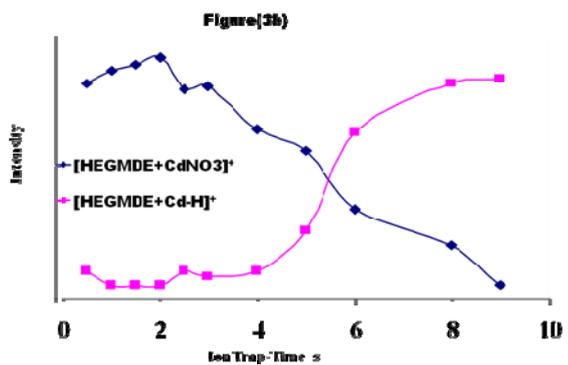
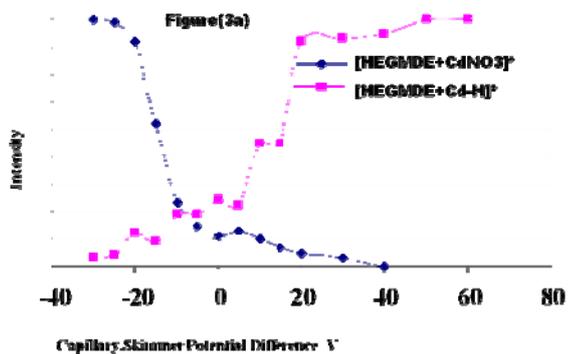


Figure 3(a) and 3(b): The voltages applied to the capillary/skimmer ion optics, and the trap time in the hexapole ion trap of the HEGMDE/ Cd(II) complexes respectively.

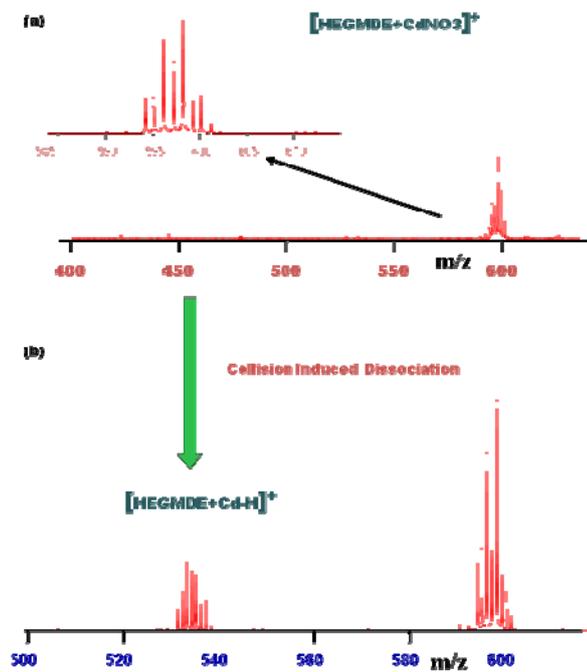


Figure 4. ORBITRAP FT ICR (TD) mass spectra of HEGMDE/Cd(NO₃)₂.H₂O