



# Chemical modification of the matrix gas: Comparison experiments with ESI-MS and ESI-IMS-MS



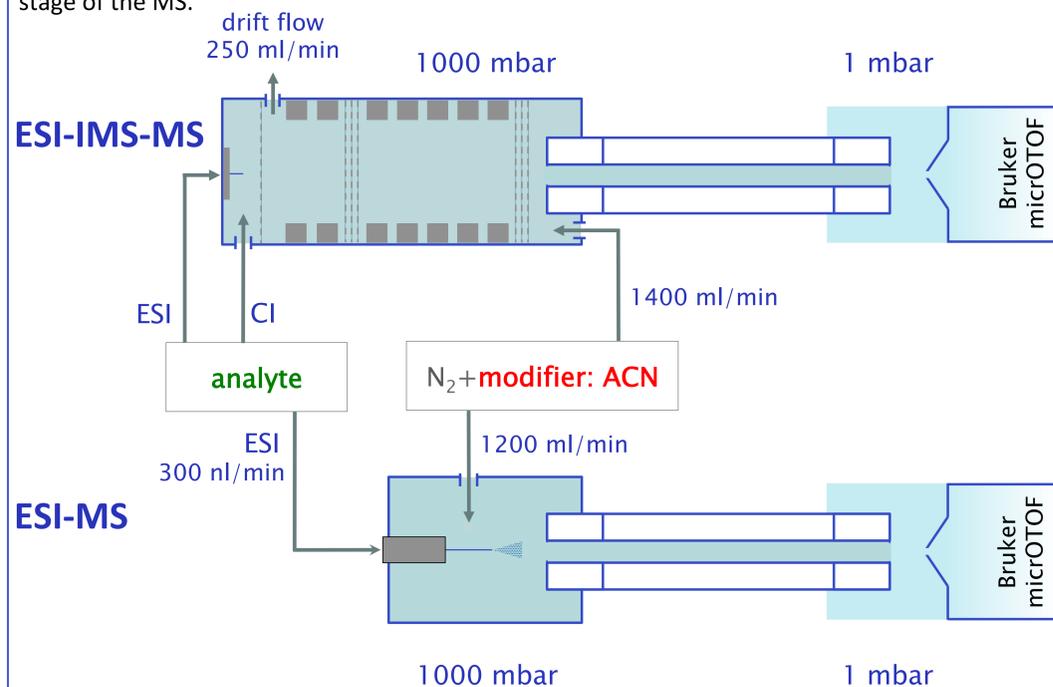
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## Experimental Setup

**ESI-IMS-MS:** The high-resolution ambient pressure drift tube IMS system is coupled via a gated transmission stage to the MS. In addition to ESI, a Corona discharge (APCI) is available as ionization method. Due to the three-grid ion gate, measurements can be performed in the IMS mode or the selective IMS-MS mode. In the selective IMS-MS mode single ion peaks of the ion mobility spectrum are transferred to the MS.

**ESI-MS:** The custom nano ESI source is mounted directly onto the transfer capillary of the MS. The source gas (including the modifier) is thus quantitatively transferred to first differential pump stage of the MS.



## Methods

**MS:** micrOTOF II (Bruker Daltonics, Bremen, Germany)

**ESI-MS:** Custom nano Electro spray Ionization [1]

ESI-solution: 1 mmol/l analyte in ACN:H<sub>2</sub>O (1:1) + 0,1 % formic acid (FA)

**IMS-MS:** Custom high resolution ambient pressure drift tube IMS [2] with Corona (CI) and electro spray (ESI) ionization source. ESI-solution: ACN:H<sub>2</sub>O (1:1) or MeOH:H<sub>2</sub>O (1:1) + 0.0001 % formic acid

**Gas Supply:** Boil-off nitrogen (Linde Gases Division, Pullach, Germany), all gas flows are controlled by mass flow controllers (MKS Instruments, Germany; Bronkhorst, Netherlands)

**Chemicals:** Chemicals were purchased from Sigma Aldrich, Germany, and used without further purification: 1,2-diaminoethane (EDA), 1,3-diaminopropane (PDA), 1,5-diaminopentane, 1,8-diaminooctane, formic acid, acetonitrile (ACN) and water (H<sub>2</sub>O)

**Calculation:** Gaussian16 with GaussView 6.0.16 for geometry optimization and thermochemistry, calculations were performed at the B3LYP-GD3BJ/def2-TZVPP level of theory. MobCal-MPI [3] code for collision cross section (CCS) calculations.

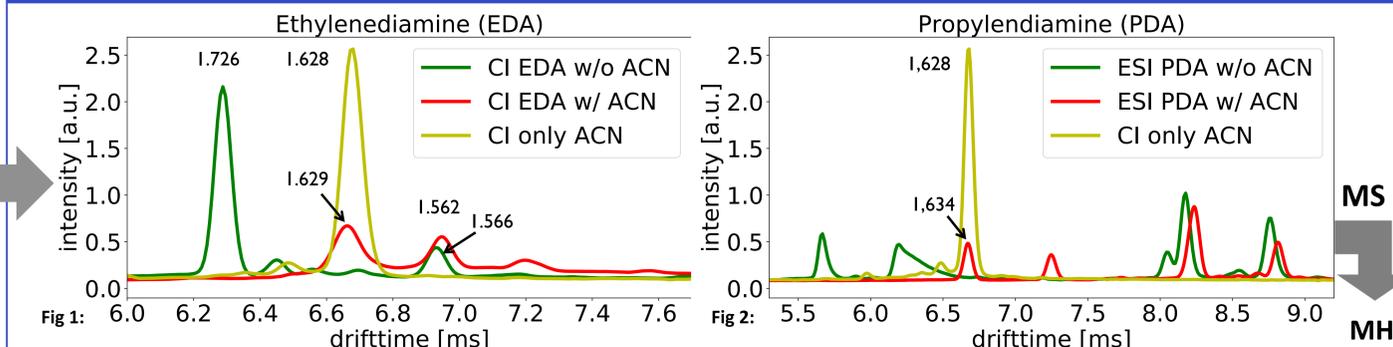
## Introduction

The ion chemistry and therefore the ionization mechanisms prevailing in atmospheric pressure ionization, e.g. chemical ionization (CI) or electro spray ionization (ESI), are dominated by cluster reactions between ions and polar compounds, e.g. LC solvents. Especially in ESI - and even in nanoESI - the sprayed solvents are present in sufficiently high gas phase mixing ratios\* that protonated ions are solvated by numerous solvent molecules. These ion-solvent interactions and their impact on the observed ion distribution of diamines were studied with the ESI-MS setup [4] and theoretically [5]. To derive a better understanding of the highly dynamic ion-solvent cluster equilibria, ESI- and CI-IMS-MS comparison experiments with diamines as analytes and ACN as modifier were performed.

\*Spraying a ACN:H<sub>2</sub>O (1:1) solution with a flow rate of 300 nl/min in a API source flushed by 1 L/min N<sub>2</sub> results in a gas phase mixing ratio of 70 ppmV for ACN and 200 ppmV for H<sub>2</sub>O.

See also: TP266 and MP300

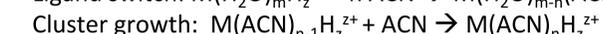
## ESI-IMS-MS & CI-IMS-MS



The black numbers in the IMS indicate the reduced mobility  $K_0$  of the related peak in cm<sup>2</sup>/Vs.

In IMS-MS mode (peak snipping) only MH<sup>+</sup> and (ACN)<sub>2</sub>H<sup>+</sup> ions are detected; unequivocal peak identification is not possible, though.

In the presence of ACN the ion mobilities of the observed RIP and analyte peaks decrease. The elevated ACN gas phase concentration alters the cluster chemistry via:



For EDAH<sub>2</sub><sup>2+</sup> the  $\Delta G$  values of the ligand switch and cluster growth reactions ( $z=1$ :  $n=m-1-4$ ,  $z=2$ :  $n=m-1-6$ ) were calculated. All reactions considered are exergonic and therefore thermodynamically favorable.

The CI spectrum of ACN (yellow trace,  $K_0=1.628$ ) shows one major peak, which represents the "thermodynamic sink" of the ACN system at a water mixing ratio of 3 ppmV: most probably H<sub>3</sub>O(ACN)<sub>3</sub><sup>+</sup>.

## ESI-MS: Experiment and Calculations

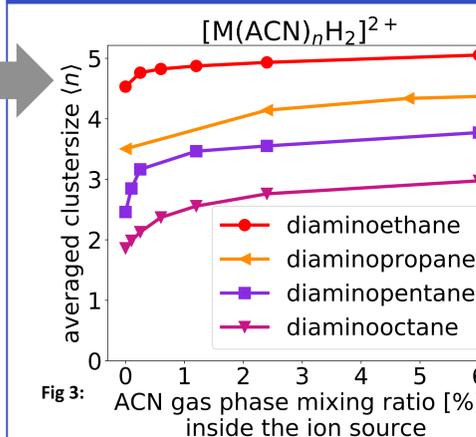
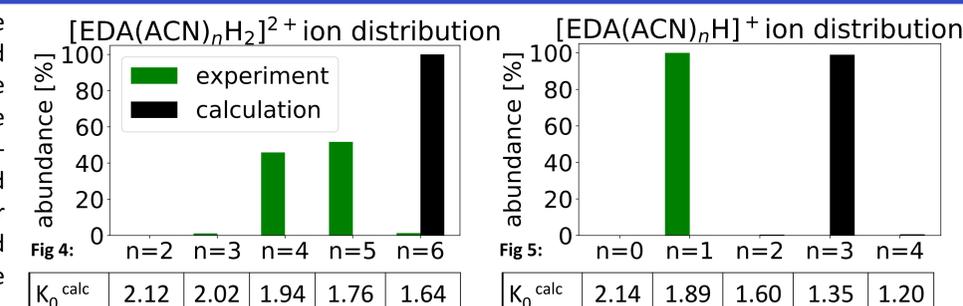


Fig 3: averaged cluster size (n) vs ACN gas phase mixing ratio [%] inside the ion source

The doubly protonated diamines are clustered with ACN. The observed cluster size depends on the ACN gas phase mixing ratio and on the length of the C-chain between the protonated amine functions (cf. Fig 3). Regarding the singly protonated diamines, the first ACN cluster  $[M(\text{ACN})_1\text{H}]^+$  is the sole cluster species detected - even at very high ACN mixing ratios. Fig 4 and 5 show the calculated (thermodynamic equilibrium) and measured ion distributions for EDA at 70 ppmV ACN. As expected, the experimental averaged cluster size value is smaller than the calculated value because declustering processes occur during the ion transfer to the detector. In contrast to ESI-MS, the mass spectra in the IMS-MS experiments show no cluster species, as expected: A sufficient transmission from the IMS to the MS requires stronger ion focusing and acceleration than in the ESI-MS setup - resulting in total declustering.



Comparing the calculated  $k_0$  values of EDA(ACN)<sub>n</sub>H<sup>+</sup> with the experimental  $K_0$  in Fig 1, the first peak (green trace,  $K_0=1.726$ ) may correspond to the EDA(H<sub>2</sub>O)<sub>m</sub>H<sup>+</sup> cluster system and the second peak (green trace,  $K_0=1.566$ ) to the EDA<sub>2</sub>(H<sub>2</sub>O)<sub>n</sub>H<sup>+</sup> cluster system:  $K_0^{\text{calc}}(\text{EDA}(\text{H}_2\text{O})_4\text{H}^+)=1.77 \text{ cm}^2/\text{Vs}$ ;  $K_0^{\text{calc}}(\text{EDA}_2(\text{H}_2\text{O})_2\text{H}^+)=1.62 \text{ cm}^2/\text{Vs}$ .

## Summary

- In ESI-MS intense clustering with the modifier ACN is observed for the doubly protonated diamines  $M(\text{ACN})_n\text{H}_2^{2+}$  ( $n=1-6$ ) but only the  $M(\text{ACN})_1\text{H}^+$  species for the singly protonated diamines
- No  $M(\text{H}_2\text{O})_m\text{H}_z^{z+}$  cluster species are detected in ESI-MS  
→ clustering with ACN is thermodynamically favored
- IM spectra show both strongly and weakly responding (shifting) peaks to ACN modifier addition
- Characterization of the individual IM peaks was not possible  
→ declustering and fragmentation during ion transmission
- CCS and  $K_0$  values for the EDAH<sup>+</sup>, EDAH<sub>2</sub><sup>2+</sup> and EDA<sub>2</sub>H<sup>+</sup> cluster systems were calculated

## Literature

- [1] M. Thinius, M. Langner, H. Kersten, T. Benter, Impact of chemical modifiers on the cluster chemistry during electro spray ionization, *Proceedings of the 63th ASMS Conference on Mass Spectrometry and Allied Topics*, San Antonio, TX, USA (2016)  
DOI: 10.1007/s13361-018-2045-4
- [2] DOI: 10.1039/C8AN02150C
- [3] DOI: 10.1039/C8AN02150C
- [4] C. Polaczek, A. Haack, M. Thinius, W. Wissdorf, H. Kersten, T. Benter, Ion-solvent interactions in nanoESI-MS: Characterization of charge depletion and charge conservation (supercharging) processes, *Proceedings of the 65th ASMS Conference on Mass Spectrometry and Allied Topics*, San Diego, CA, USA (2018)  
DOI: 10.1021/jasms.9b00045

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