Introduction

The HiKE-IMS allows experiments at reduced electric field strengths (E/N) also prevailing in IMS or in the ion optics of LT-MS.

Previously, we successfully modeled the drift time of proton bond water clusters in an HiKE-IMS inducing chemical transitions between clusters (see figure 1).3

In this work the effect of chemical modification of the drift gas in an HiKE-IMS is studied. Chemical modification is the deliberate introduction of effective clustering agents to the gas which significantly change the mobility of many analytes. This technique is frequently used in DMSIP and IMSIP to improve separation efficiency.

HiKE-IMS (Leibniz University Hannover):

- Method is based on a classic drift tube IMS
- Ion separation in the drift tube (L = 30.65 cm), which is coupled to the reaction tube (separated by a shutter grid assembly)
- Analytes (Acytacetitrile (ACN) and 1,3-Diaminopropane) are added in pure nitrogen to the reaction tube and are ionized with a corona discharge
- Nitrogen is used as modifiable matrix drift gas in the reaction tube
- Operated at low pressure (20-30 mbar) and a temperature of max. 45 °C (min: RT)

ACN: Temperature and water dependency

Even without additionally modified most of the analyte specific signals exhibit rising red mobility with rising E/N. Thus, another clustering species must be present. This is most probably residual water in the drift gas.

Note the negative dependency of the ACN-species (see figure 7), which supports this presumption. The residual water concentration seems to be much higher than any modifier concentration; thus the shifts of figure 6 are explainable by water-analyte clustering.

Conclusion

- Similarly to the water cluster system, the chemical dynamics of other small polar molecules are of great importance in IMS.
- Both, the modifier concentration present in the drift gas and the extent of analyte-modifier cluster chemistry is important for an enhanced separation efficiency.
- Since water is a strong clustering agent, a modifier has to be present in at least comparable concentrations to yield a noticeable modification effect.
- A qualitative classification of the modifier potential is possible.

Cluster dynamics and stabilities in comparable setups (DMS or ion optical stages) can be investigated with present experimental and simulation approaches.

Even one single analyte can exhibit complex chemical cluster dynamics. Such a system becomes rapidly extremely complex when additional active analyte species are present.

A deeper analysis and assignment of all signals seems to be impossible without a suitable IMS-MS-coupling or comparable experimental setups.

Experimental

- Setup of an HiKE-IMS system to selectively analyze the drift signals
- Detailed investigations of modifying processes and the significant parameters
- Simulation of an HiKE-IMS operating stage without changing the ion-transport
- Extension of the existing simulation code for more complex systems

Simulating clusters in an HiKE-IMS allows a more complete and efficient understanding of the effect of chemical modification on the overall clustering in the drift gas.

ACN gas modification with ACN

Figure 6: Mobility of the three main signals of ACN is dependent on the drift field strength with different modifier raising ratios (ACN) in the drift gas

Increasing the water concentration in the drift gas results in a similar behavior as decreasing the temperature. The mean cluster size increases with rising dew point and as result the red mobility is decreasing. Only clusters with water (i.e., exhibiting a slope close to zero) remain unchanged.

Note that all clustering effects decrease at much higher red. field strengths.

Comparative observations were made with acetone and methanol as analyte and modifier.

AC: Introduction and Cluster Dynamics in High Kinetic Energy IMS (HiKE-IMS)

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Drifter gas modification with ACN

With Acycctetitrile (ACN) as analyte and modifier two main signals are observed as shown in figure 3. The notified plateau between the signals, which indicates a chemical connection between both species (cluster ‘switch’), is also seen in figure 4. The noticeable step between 60 and 70 Td indicates a change in the clustering state.

The exemplary mass spectra shown in figure 5 demonstrate the clustering behavior of ACN with itself and with water. This suggests that the plateaus in the IMS-spectra shown in figure 3 as well as the steps in the graphs showing red mobility data are caused by similar chemistry as the previously observed cluster chemistry of water.

Note the existence of mixed water-ACN-clusters.

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