

Effects of physical and chemical interactions in ion mobility spectrometry (IMS) depending on the reduced field strength

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Introduction

Ion separation exploiting the electrical mobility K is a common method in modern analytical chemistry. Techniques as differential ion mobility spectrometry (DMS) build on mobility changes between molecular states of different energy^[1] while the “classical” ion mobility spectrometry (IMS) utilizes the absolute ion mobility.^[2]

Previous results of DMS experiments point out that dynamic clustering/declustering processes are often the root cause for ion separation with this method.^[3] The clustering of analyte ions with background water^[2] or with modifiers, which are deliberately introduced in the drift gas^[4] are typical chemical processes in drift tube IMS known from literature. The separation of enantiomers was observed by using a chiral modifier, which is also a clear indication of clustering.^[4] However, there is no induced declustering by increased effective ion temperature as in DMS. Therefore, one could assume that statistical chemical systems are observed in IMS, which is incorrect. Even without an oscillating electric field, there is still a dynamic reaction system of ions and neutrals. We present experimental results generated with a High Kinetic Energy IMS (HiKE-IMS), which is characterized by a high resolution and increased effective ion temperatures.^[5] The results are verified by simulations, which can be transferred to similar conditions in MS-systems.

Experimental^[5]

- The HiKE-IMS (Leibniz University Hannover) is based on a classical drift tube IMS.
- Analytes are induced in pure nitrogen to the reaction tube and are ionized by means of a corona discharge.
- The ions are separated in a 30.65 cm long linear drift tube with nitrogen as drift gas and a pressure of about 20 to 30 mbar. Chemical modifiers can be added to the drift gas.

→ High reduced field strengths (> 120 Td) and the direct observation of cluster transitions (high resolution) are possible.

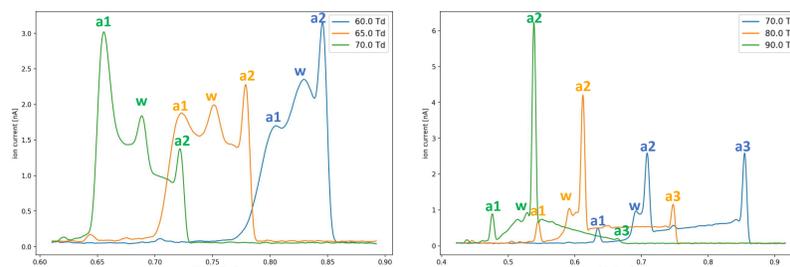
- A particle based kinetic code^[6] (customized version of a Monte Carlo method) is used for simulations.

Simulations

Based on the assumed highly dynamic cluster system the reduced field strength dependency of the water-RIP drift time was simulated (fig. 6). Apart from a small shift of the absolute values and the missing pre-RIP, which was not simulated at all, both results are basically identical. Note the broadening of the peaks at the cluster transitions in both spectra.

Figure 6: Comparison of experimentally generated water-RIP (top) and simulations (down) of the same system ($T \approx 322.15$ K; $DP \approx -35$ °C) in dependence of the reduced field strength

Effect of clustering processes



Upon rising the reduced field strength, the ion current is “shifting” from one signal to another, while a plateau spans between both peaks (see fig. 1). This is explained by a cluster transition at specific settings.

The plateau strongly suggests an underlying dynamic reaction system. It is likely that this observation is the result of a complex transition towards smaller clusters (change of the statistic distribution of chemical species).

Note the effect is observed with different systems of small analytes.

Figure 1: Cluster-transition processes at three representative reduced field strengths. The typical signals of the water-system (RIP) is marked with w and the analyte-specific signals with aX; left: ACN (0.9 ppmV in the reaction tube and 1.6 ppmV in the drift gas), right: Acetone (1.3 ppmV in reaction tube and 2.2 ppmV in the drift gas)

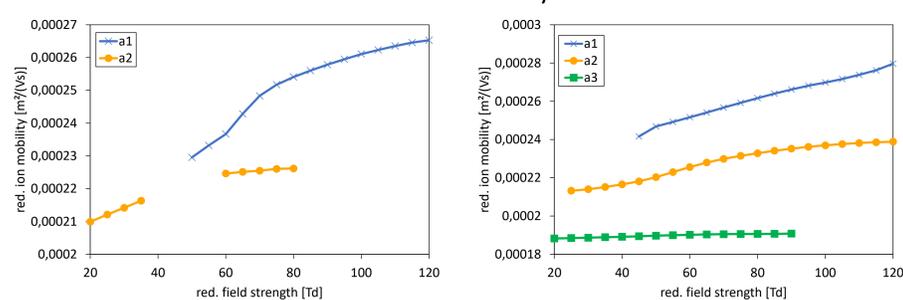


Figure 2: Effect of increasing reduced field strength on the reduced ion mobility of the typical analyte-specific signals defined in figure 1; left: ACN (0.9 ppmV in the reaction tube and 0.6 ppmV in the drift gas), right: Acetone (1.3 ppmV in reaction tube and 2.2 ppmV in the drift gas)

Ion mobility K : $v_d = K \cdot E$

v_d : drift velocity
 E : electric field strength

Reduced ion mobility K_0 :

$K_0 = K \cdot \frac{p \cdot T_0}{p_0 \cdot T}$
 $T_0: 273.15$ K
 $p_0: 101325$ Pa

The reduced ion mobility in dependence of the reduced field strength also suggests complex clustering/declustering processes (probably with background water).

Note that the acetone specific signal with the lowest mobility (right, a3) seems to be independent from the energetic situation, what is known for the acetone dimer by former AP-IMS measurements.

Water cluster system

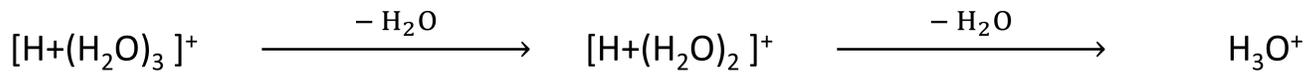
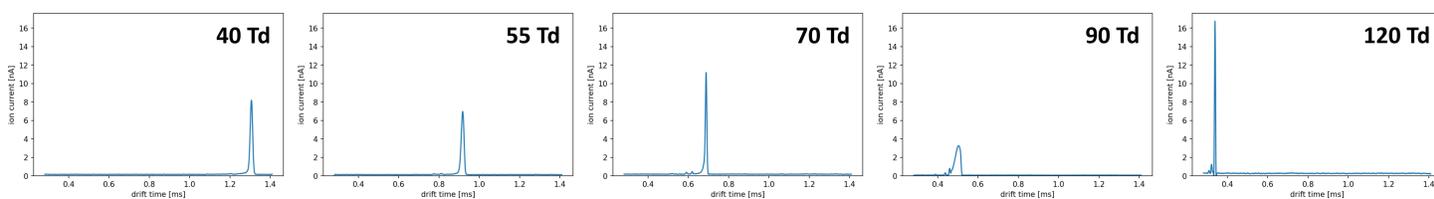


Figure 3: Experimental HiKE-IMS-spectra in dependence of representative reduced field strength (from left: 40 Td, 55 Td, 70 Td, 90 Td and 120 Td) and the main species in the postulated declustering process.

With increasing reduced field strength, the signals of the pure water clusters (“RIP”) exhibit a stepwise, significant broadening of the observed peaks. This effect coincides well with the simulated

cluster transitions from the third to the second water cluster and from the second cluster to H_3O^+ even if the conditions are not entirely identical (see fig. 4). The clusters are not entirely

separated in the transition, even with the high resolution of the HiKE-IMS. Note the pre-RIPs at lower drift times relative to the water-RIP, which origins have not been finally identified.

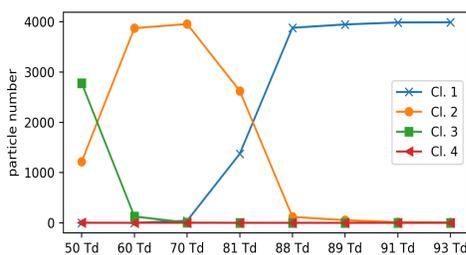


Figure 4: Simulated cluster distribution of water in dependence of the reduced field strength

The reduced ion mobility is decreasing with increasing humidity (see fig. 5) due to an increasing average cluster size. In addition, there is a noticeable shift of the cluster transitions, which are clearly visible by the shifts of the drops in the modulation of the maximum ion current at elevated reduced field strength.

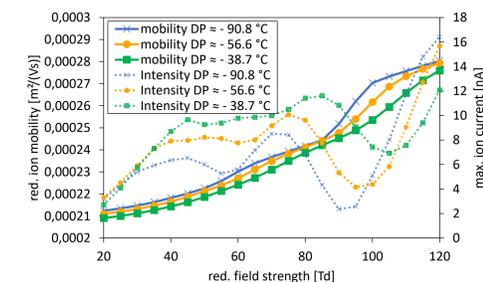


Figure 5: Effect of increasing reduced field strength on the reduced ion mobility and the maximum ion current of the water-RIP at different dew points (DP) in the drift gas

Conclusions

- Clustering mechanisms have to be considered as a general phenomenon in IMS systems. Basic information is discussed in the literature.
- The existence of dynamic cluster transitions is demonstrated for various systems comprised of low molecular weight analytes.
- A basic simulation of a dynamic reaction system reproduces the experimental result very well.
- The chemical and physical interactions of

ions and neutrals cannot be ignored even at static conditions. Thus, there are few, if any, pure analyte-peaks in a typical IMS spectrum of reactive small molecules.

- The interactions are governed by parameters as temperature, humidity and concentrations of gas-phase modification agents.
- The basic reaction dynamics investigated in HiKE-IMS can be transferred on other systems, e.g. DMS and API MS.

Literature

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