

# Chemical kinetic and ion transport simulations: Temperature dependence of ion mobility and its impact on cluster equilibria

## Introduction

Ion separation in Differential Mobility Spectrometry (DMS) is driven by the dependency of the ion mobility (K) on the electric field strength [1, 2]. Previous results show that the formation of ionmolecule clusters are one of the main causes for the occurrence of differential ion mobility in DMS [1, 3]. Another is the decrease of mobility of individual cluster species with increasing field strength due to the interaction of ions and background gas ("Hard-Shell effect"). Recent simulations of a DMS stage excluding hard shell effects were in good qualitative agreement with experimental data but also showed systematic differences from experiments [3]. We present a refined version of the numerical model, considering the field dependence of the ion mobility of the individual cluster species. Experimental and numerical results for the proton bound water cluster system including variable background gas temperature are presented and discussed. Furthermore, the direct comparison between ion transport simulations in a High Kinetic Energy ion mobility spectrometer (HiKE-IMS) with experimental data allows to verify and parameterize the simulation approach.

## **Differential Mobility Simulation: Effect of individual cluster species**



**Time resolved cluster dynamics in DMS** 

## Variation of the extent of the field dependence

The ion mobility may be regarded as constant at low field conditions, but with increasing reduced field strengths, the ion mobility of each individual cluster species decreases [10]. To consider this effect, analytical fitting functions were used to model the individual mobility on the reduced field strength, where c parameterizes the strength of the hard shell effect in the linear model (c = 1 means that the mobility is half of the low field mobility at 100 Td):

$$K_{lin}(E) = K - \frac{1}{2} \frac{E}{N} c K \times 10^{19}$$
$$K_{exp}(E) = \exp(-4.4 \times 10^{-8} E) K$$

*right:* Ion mobility of the first proton bound water cluster species  $[H_3O]^+$  in dependence of field reduced strength using different fitting functions. The linear model was run with c = 0.25.

$$K_{exp}(E) = \exp(-4.4 \times 10^{\circ})$$
3 % water, 140 °C, e-field variation
$$Ieft:$$
linear
depe
chem
separ
trans

Variated strength of the hard shell effect with arly decreasing ion mobility. For low field endences of the individual cluster (low c) the nical cluster effect is dominating the ion ration. Increasing the field dependence induces a transition from Type A behavior (cluster effect) to Type C behavior (hard shell effect).

## Variation of the water mixing ratio

20

compensation voltage (\

3000 -

2500

<u> ೪</u> 2000

1500

1000

-20

Decreasing the water mixing ratio yields in an  $\alpha$ -function, which is dominated by the cluster effect (Type A behavior). The  $\alpha$ -function for a high water mixing ratio is influenced by the hard shell effect (Type C behavior), resulting in higher compensation voltages with increasing SV. At 3000 SV there is a transition from small CV values to higher CV values with increasing water mixing ratios.

40

*right:* Dependence of the simulated CV on the SV at three different water mixing ratios with linearly decreasing ion mobility (c = 0.25) and a background temperature of 170 °C.

(linear model)

(exponential model)

$$K_{lin}(E) = K - \frac{1}{2} \frac{E}{N} d$$

**—** c = 0.25

→ c = 0.2

---- c = 0

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# Methods

## **DMS experiments:**

DMS/ MS system: SCIEX 6500 Triple Quad<sup>™</sup> with SelexION<sup>®</sup> DMS SCIEX Turbo V™ (APCI-mode) lon source: SCIEX Analyst<sup>®</sup> 1.6.2 **Data Processing:** 

## **Chemical Kinetics Simulation:**

Customized version of "RS" Monte Carlo kinetics code [4] equilibrium state simulations: Cantera 2.1.1 [5]

## **IMS experiments:**

High kinetic Energy IMS (HiKE), Field strength: 12 – 107 Td, 20 mbar background pressure [6, 7]



*left:* Time resolved cluster concentrations and mean cluster size of the proton bound water cluster system at a water mixing ratio of 0.3 % at 170 °C in a DMS separation field (SV = 3000 V).

The separation field induces large amplitude oscillations of the individual cluster concentrations and thus to the average cluster size by electric acceleration of the ions. The mean cluster size is higher in the low field phase than under high field conditions, resulting in a differential ion mobility.



linear model exponential model reduced field strength (Td) SV variation, 373 K, 3 % water --- exponential model 🔶 linear model -20 -30 compensation voltage [V] above: Dependence of the CV on the SV with both mobility

models at a water mixing ratio of 3 % at 100 °C.



Proton bound water cluster reaction system with temperature dependent rate constant [3]:

 $T_{\rm eff} = T + \frac{M(KE)^2}{2}$ M: collision gas mass сь: Boltzman constant  $'_0$ : normal temperature (273.15 K)  $K_0 = K \frac{p}{n} \frac{T}{7}$ 

The effective ion temperature in an electric field *E* is given by [2]: Reduced ion mobility (temperature and pressure normalization) [2]:

According to experimental results for the proton bound water cluster system with variated background gas temperature there is no significant temperature dependence of the ion separation. However, considering the field dependence of the individual cluster mobility in the numerical model, the simulation predicts a strong temperature dependence of the differential mobility. In contrast, ignoring the individual cluster mobility dependence on the field and the temperature dependence of the gas density, the numerical and experimental results match qualitatively (see figure on the far right)



above: Time resolved average mobility in dependence on the separation voltage and the background gas temperature without hard shell corrections (c = 0). The average cluster size decreases with increasing temperature and the average mobility increases, but the amplitude of the chemical oscillation induced by the SV is essentially independent from the background temperature

# Water Clusters in High Kinetic Energy IMS (HiKE)

HiKE is a high resolution drift tube IMS which employs high reduced field strengths up to 100 Td. The proton bound water cluster system was measured in dependence of the field strength. The exact water mixing ratio in the drift tube was unknown. Chemical kinetics simulation (Cantera) and the experimental drift times suggest a water mixing ratio of 4.9 ppmV due to the presence of mainly cluster 3 at 44 Td.



Since the drift time at 44 Td equals 1.2 ms, cluster 3 is the dominating species. The transition from cluster 3 to cluster 2 is visible between 50 Td and 70 Td. A second even more pronounced transition from cluster 2 to cluster 1 occurs in a range of 81 Td to 100 Td.

# Simulation approach

 $[H + (H_2O)_n]^+ + H_2O + N_2 \rightleftharpoons [H + (H_2O)_{n+1}]^+ + N_2$ 

Applying an AC voltage (separation voltage, SV) with an asymmetric waveform causes ions to drift on zig-zag trajectories towards one electrode of the DMS. The ion drift depends on the relative difference between the low- and high-field mobility. To balance the ion drift, a DC voltage (compensation voltage, CV) is applied, which allows selected ions to pass through the DMS stage. The simulation iteratively calculates a CV value so that the net motion of the reacting ion ensemble towards one DMS electrode vanishes.

The dependence of the CV on the SV yields information about the  $\alpha$ -function, which is defined as [2]:

# DMS Simulations: Background Gas Temperature







top left: Simulated and experimental CV dependence on the SV. For the simulation a linearly decreasing ion mobility as well as the temperature normalization was assumed (c = 0.25). The simulations show a significant temperature dependence in contrast to the experimental results.

top right: Simulated and experimental CV dependence on the SV, without consideration of the temperature dependence of the individual cluster mobilities and temperature normalization. The results surprisingly match much better with the experimental results, despite the fact that the model here ignores well known physical aspects.

*left*: Simulation of ion drift in HiKE with a simple transport model (excluding ion diffusion). These results are in very good agreement with the experimental results shown above.

at selected



50Td 89Td 60Td 91Td 💻 70Td 🛛 🔲 93Td 🔲 81Td 🚺 101Td 88Td 107Td 1500 -0.4 0.6 0.8

Transport simulation results of HiKE considering the hard sphere effect. The results of ion transport simulations with a hard sphere collision model slightly differ from the experimental results and the previous simulations results. The hard sphere model currently does not use an individual collision cross section (CSS) for each individual cluster species. This leads to a contradiction of the simulated drift times. Note that the drift time depends on the CSS. Decreasing the CSS yields smaller drift times.



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An ion with a monotonously increasing  $\alpha$ -function is defined

as Type A [8], with a monotonously decreasing  $\alpha$ -function as

Type C [8]. lons with an increasing and then decreasing  $\alpha$ -

Ion transport simulations were performed with dedicated

custom simulation programs, using established base ion

mobilities [3] and a hard sphere collision model [9].

function are defined as Type B [8].

K(E): high field ion mobility

K(0): low field ion mobility

*left*: Simulated cluster distribution in dependence of reduced field strength. Cluster 3 is the most abundant species at 50 Td, whereas at 70 Td cluster 2 is dominating. For reduced field strengths  $\geq$  88 Td only cluster 1 is present. Thus the observed average ion mobility increases with increasing reduced field strength.

*left*: Simulation of ion transport including a hard sphere effect with a mean ion collision cross section of 0.8 nm.



*left*: Simulation of ion transport including a hard sphere effect with a mean ion collision cross section of 1.0 nm.

# **Conclusions & Outlook**

## Conclusions

- The hard shell effect modeled by the employed simple analytical models is generally overestimated as compared to experimental results.
- Both, the cluster effect and hard shell effect are required to model ion transport and chemical dynamics in a DMS stage to arrive at meaningful data.
- The experimentally observed dependence of the CV on the background gas temperature was not reproduced by the DMS simulations, probably due to an insufficient hard shell effect model.
- HiKE simulations are in a good qualitative agreement with the experimental results.

## Outlook

- Improvement of the hard shell fitting function to describe the field dependence of the individual cluster mobilities better.
- Adapt a gas collision/ diffusion model to the characteristics of the DMS simulations and consider space charge effects via a Barnes-Hut method
- Estimate space charge effects in a HiKE with the improved simulation method
- HiKE IMS experiments with known water mixing ratios and comparison with numerical results

## Literature

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