

# Is differential mobility chemically driven? Evidence and simulations for chemical effects as a primary separation factor in DMS



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## Introduction

The ion separation in Differential Mobility Spectrometry (DMS) relies on the dependence of the ion mobility ( $K$ ) on the electric field strength [1,2]. There are several mechanisms, which lead to differential mobilities by physical as well as chemical interactions between analyte ions and gas matrix components [2, 3, 4].

Among those, the formation of ion-molecule clusters with background gas constituents are the primary reason for the occurrence of differential mobility for chemically active analyte molecules [5]. Energy dependent collisions lead to significant changes in the cluster size and the resulting experimentally observed ion mobility.

We present experimental evidence and simulation results, which show the complex chemical dynamics in a DMS cell and the significance of chemical effects for differential mobility.

## Methods

### DMS / MS Experiments:

**DMS / MS System:** Sciex 5500 QTRAP with SelexION DMS  
**Ion Source:** Sciex Turbo V ESI Ion Source  
**Data Processing:** Sciex Peak View 1.2.2.0

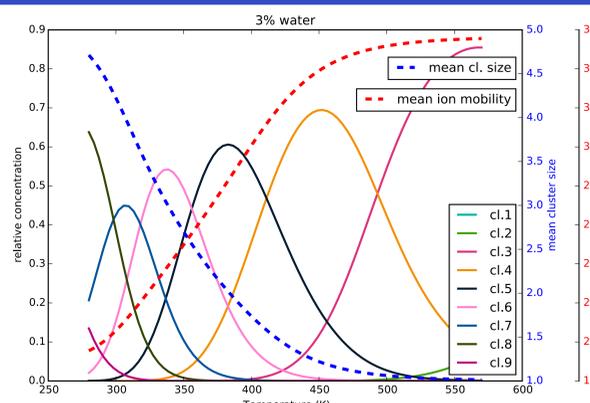
### Chemical Kinetics Simulation:

- non equilibrium state DMS cell simulations: Customized version of "RS" Monte Carlo kinetics code [6]
- equilibrium state simulations: Cantera 2.1.1 [7]

### Ab initio calculations:

- Gaussian 03

## Proton Bound Water Cluster System Dynamics



### Simulation approach

#### Water cluster reaction system:



#### Ion temperature and temperature dependent reaction rates:

The effective ion temperature  $T_{eff}$  in an electric field  $E$  is given by:

$$T_{eff} = T + \frac{M(KE)^2}{3k_B} \quad k_B = \text{Boltzmann constant}$$

$M$  = collision gas mass

The cluster building (forward) reaction is considered as collision controlled [6], thus its rate  $k_f$  is calculated from the collision theory:

$$k_f = \sigma \sqrt{\frac{16RT}{\pi\mu}} \quad \sigma = \text{collision cross section}$$

$\mu$  = reduced particle mass

The reverse reaction rate is calculated from the equilibrium constant  $K$ , which is given by the Gibbs enthalpy  $G^0$  of the clustering reaction:

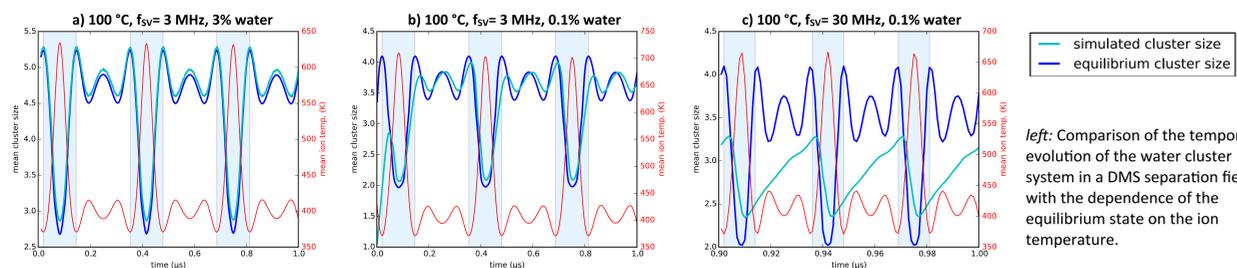
$$G^0 = -RT \ln(K)$$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \Delta H^0 = \text{Reaction Enthalpy}$$

The temperature dependence of the equilibrium constant is estimated using the van't Hoff equation:

above: Temperature dependent equilibrium state of the water cluster system at a water mixing ratio of 3%. The clusters become smaller and more mobile with increasing temperature.

## Chemical oscillation due to separation field: Equilibrium state and relaxation

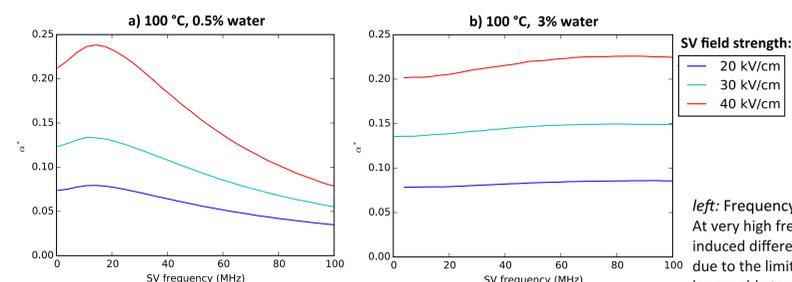


The acceleration in the oscillating separation field leads to an oscillating effective ion temperature in a DMS cell. This temperature oscillation induces chemical oscillation in the reacting cluster system, which leads to oscillating mean cluster sizes and thus cluster mobilities.

The displacement of the chemical system from its equilibrium state at a given temperature depends on the oscillation frequency and water concentration in the background gas. If the water concentration is very high (a) the chemical system follows the temperature without noticeable delay, i.e. exhibits the maximum displacement amplitude and is in phase with  $T$ .

With low water concentration (b), significant phase and amplitude changes become observable. With low water concentration and high separation field frequency (c), relaxation of the chemical system in the low field phase is significantly hindered, which results in a different temporal cluster size function.

## Frequency dependence:



The limited reaction rates of the cluster formation and decomposition reactions lead to a significant frequency dependence of the chemically induced differential mobility function  $\alpha^*$  defined as:

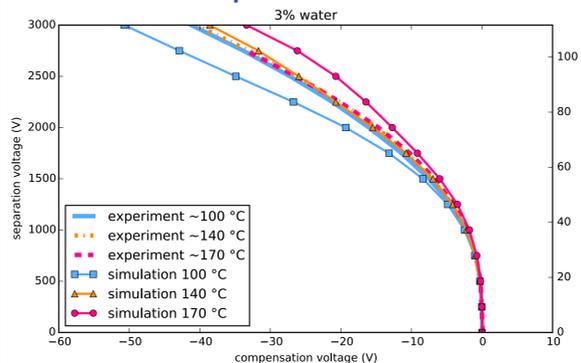
$$\alpha^*(E) = \frac{K_c(E)}{K_c(0)} - 1$$

with  $K_c$  as the chemically induced cluster ion mobility.

left: Frequency dependence of  $\alpha^*$  for the proton bound water cluster system. At very high frequencies (> 1 GHz) of the separation field (SV) the chemically induced differential mobility vanishes entirely, even for high water mixing ratios, due to the limited rate of the cluster formation reaction. The system is then no longer able to adjust accordingly from the high field phase.

## Separation / Compensation Voltage

### Water cluster: Experimental validation

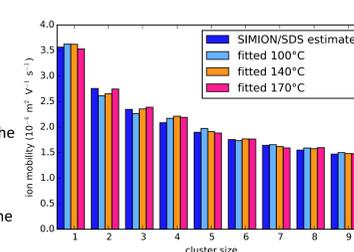


above: Dependence of the simulated and experimental compensation voltage (CV) on the separation voltage (SV) for the proton bound water cluster system signal at three different background gas temperatures.

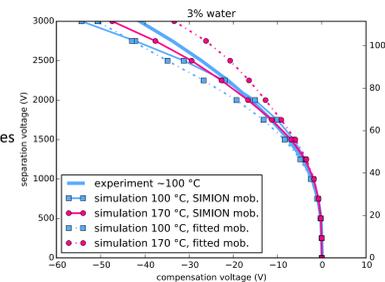
In the simulation, the mobilities of the individual cluster species were the mean values of the three "fitted" ion mobilities for the background gas temperatures presented on the right. There is clearly a not yet resolved temperature dependent divergence between simulation and experiment, potentially resulting from the collision energy dependence of the individual cluster species mobilities.

### Individual cluster ion mobilities:

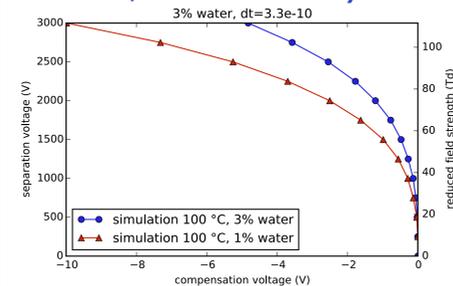
right: The simulation of the differential ion mobility in a DMS experiment requires the ion mobilities of the individual clusters ( $K_i$ ) which are only available as estimated values. Variation of the  $K_i$  values to minimize the difference between the simulated and the experimental CV function leads to "fitted"  $K_i$  vectors. The observed variation is well in the uncertainty of the originally estimated values, obtained from the statistical diffusion algorithm implementation in SIMION.



right: Effects of the variation of the individual cluster mobilities. With the initial ion mobilities estimated by SIMION / SDS there is a systematic divergence of the simulation, which predicts too high compensation voltages with increasing separation voltage.



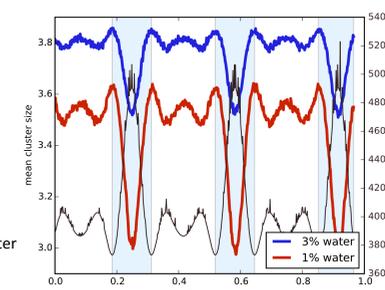
### Acetone / Water cluster system:



With similar assumptions as in the proton bound water cluster case, a set of temperature dependent rate constants for the clustering reactions of acetone with water was derived from ab-initio calculations [8]. This set of data in combination with estimated ion mobilities from SIMION / SDS was used to simulate the dynamics of the acetone / water cluster system.

left: Simulated compensation voltage of the acetone / water cluster system.

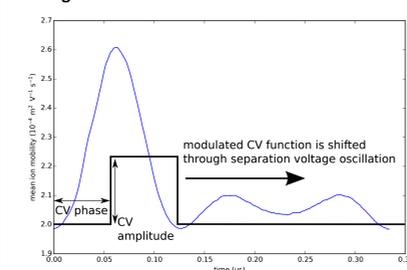
right: Oscillation of the acetone / water cluster size with the separation field oscillation.



## Outlook: Time resolved ion mobility measurements with DMS

### Basic idea:

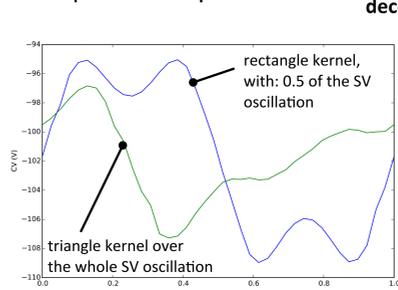
Modulated compensation voltage with variable phase relative to the separation voltage



The ion mobility oscillates with the separation voltage, which applies also to the distance an ion is transported by the CV. If the compensation voltage is also modulated, it is possible to determine the ion mobility function by varying the phase between the SV and modulated CV function.

### Measurement result:

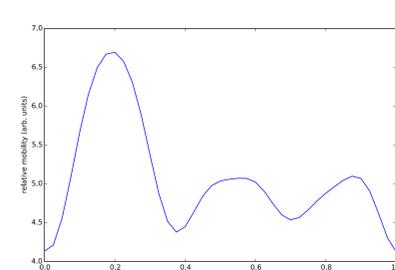
Modulated compensation voltage in dependence of CV phase



The result of such a measurement would be a compensation voltage modulated by the CV phase. This function is the convoluted result of the ion mobility function and the applied CV modulation function ("kernel"). Different kernels therefore produce different primary results.

### Reconstructed result:

Relative, time resolved ion mobility function deconvolution



Mathematical deconvolution yields a reconstructed, relative ion mobility function. Absolute determination of the ion mobility requires non-differential ion mobility measurements.

## Conclusions

- The dynamics of temperature dependent clustering is found to be the primary mechanism leading to differential ion mobility of the water cluster system
- Numerical simulation of the water cluster dynamics and the ion transport in a DMS cell is in good agreement with experimental results
- The mobilities of the individual cluster species are a significant source of uncertainty and future development should focus on this aspect of the simulation
- Simulation of the proton bound acetone / water clusters predicts a similar but less pronounced differential mobility
- At common analytical conditions (e.g. ESI conditions) the investigated cluster systems are essentially in local chemical equilibrium over the whole SV oscillation
- The simulated cluster dynamics shows a significant dependence on the SV frequency. At very high frequencies (GHz region) the chemically induced differential mobility vanishes due to the rate limitation of ion molecule reactions
- By modulating the compensation voltage, time resolved DMS experiments are possible, which allows the measurement of the time resolved relative ion mobility
- Time resolved measurements and frequency variation would allow further validation of the simulations and insights into the fast cluster chemistry of chemically active analytes

## Literature

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