

SELECTIVE ION-NEUTRAL CLUSTERING TO ENHANCE ION MOBILITY SEPARATION FACTORS

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INTRODUCTION

- Discrete interactions between ions and a homogenous, inert buffer gas under the influence of a weak electric field provide a solid foundation for ion mobility theory, but such conditions do not always promote optimal separations between ion populations.
- Buffer gas dopants are routinely used in field applications of IMS to promote specific types of ion chemistry and aside from a few notable reports,¹ little effort has been devoted towards their use in altering separation factors.
- Provided the correct input parameters a detailed model for the selective interaction between drift gas modifiers is possible via the method described by Rawat et al.²

AIMS

- Assess the capacity of drift gas modifiers to alter separation factors for analytes possessing nominally the same reduced mobility.
- Evaluate the reproducibility of altered separation factors for their potential use in operational settings.
- Identify trends in mobility shifts as a function a chemical functional group class.

METHODS

- A dual gate ion mobility cell (ExcellIMS, MA3100) with an integrated Faraday plate detector interfaced to a Thermo LTQ linear ion trap MS was used for all measurements.
- Mass-selected mobility spectra were obtained by frequency encoding the mobility data using the approach by Morrison et al.³
- Drift gas modifiers were introduced into the primary drift gas inlet via a glass capillary coupled to a temperature controlled GC injection liner. Flow rates of each modifier were introduced using a syringe pump at rates of 5 to 160 $\mu\text{L/hr}$.
- The drift gas modifier mixing chamber was held at nominally the same temperature as the mobility drift cell at 175 $^{\circ}\text{C}$.
- Analyte solutions comprising of DMMP (2.3 μM), and MPA (10 μM) were electrosprayed into the desolvation region of the instrument using custom ionization stage at flow rate of 2 $\mu\text{L/min}$.

RESULTS

Using a mixtures, representing a class of organophosphates, the data presented illustrate the ability of the drift gas modifier to alter separation factors in the ion mobility domain. In some cases, use of the modifier shifted drift times by as much as 20% compared to nitrogen and previously unresolved species (i.e. DMMP and MPA) could be resolved. Observations worth of note also include a discrepancy between the relative intensities of the arrival time distributions and the range of m/z values recorded. These data suggest API declustering which prompts questions regarding the range of clustered states in the mobility domain. Finally, different impacts on mobility shifts are possible as a function of chemical class demonstrating the potential for this approach to selectively alter separation factors in a reproducible fashion.

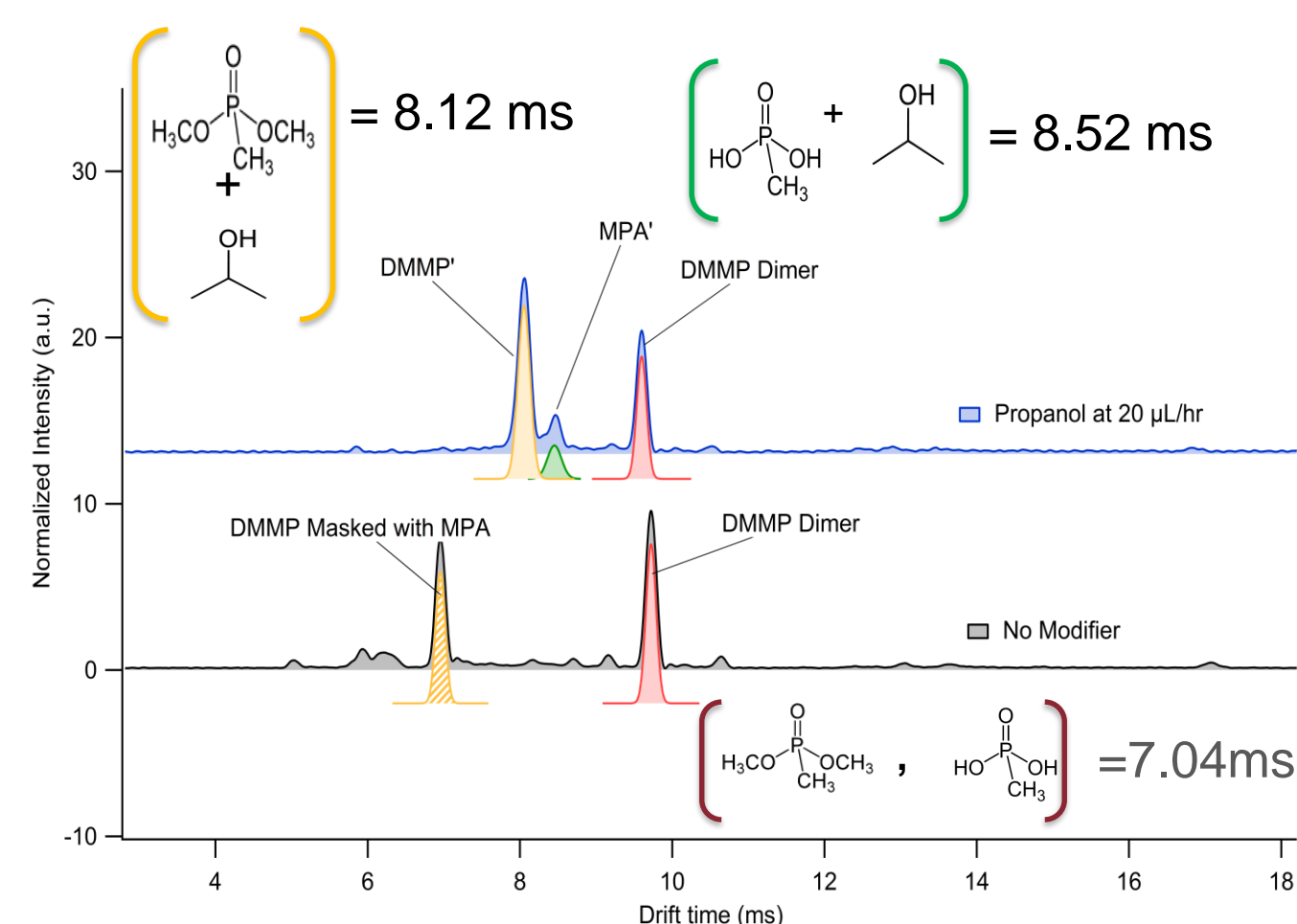


Figure 2. Faraday plate ion mobility spectra with (top trace) and without (bottom trace) 2-propanol as a modifier. The offset peaks were m/z identified using the instrument shown in Figure 2.

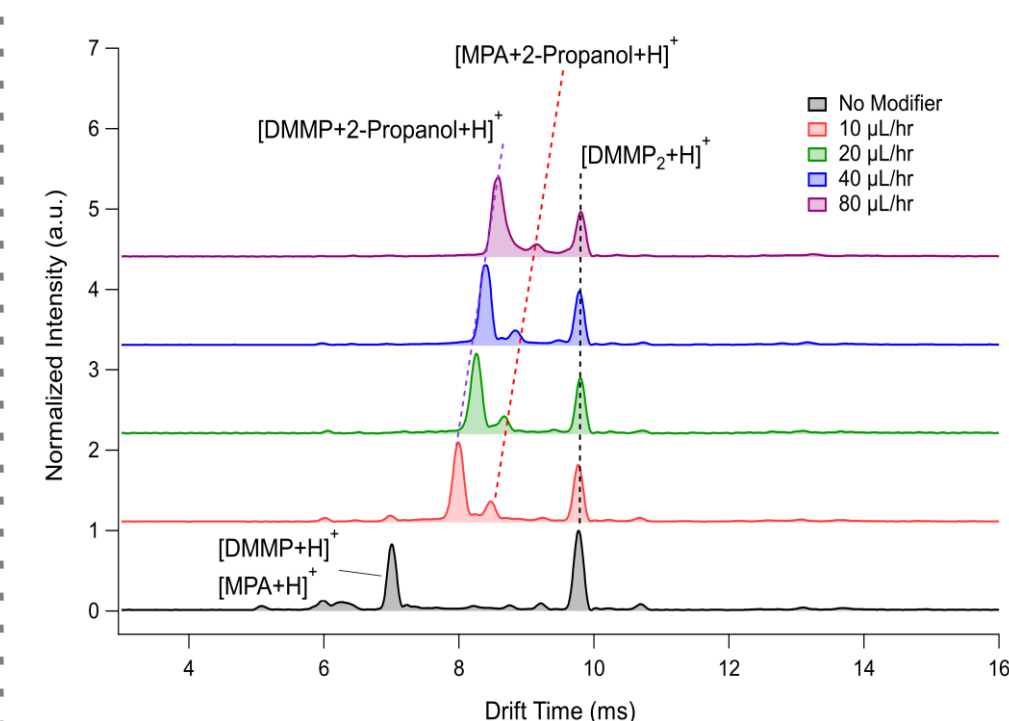


Figure 3. Mobility separations of DMMP and MPA as a function of increasing drift gas modifier concentration. The stability of the proton-bound dimer of DMMP compared to the MPA and DMMP monomers illustrate the selective interactions between the ion populations and the modifier.

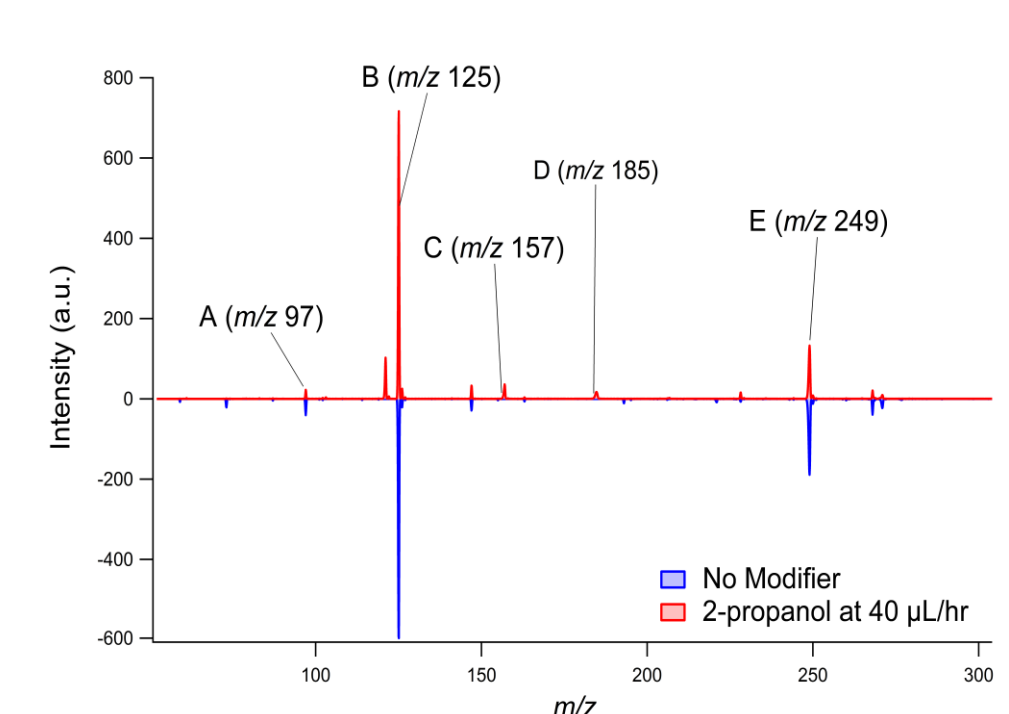


Figure 4. Composite mass spectrum for the separations of DMMP and MPA. Comparing the relative intensities between the mass and mobility domains illustrates that the clusters, though stable in the mobility domain, do not fully survive the API.

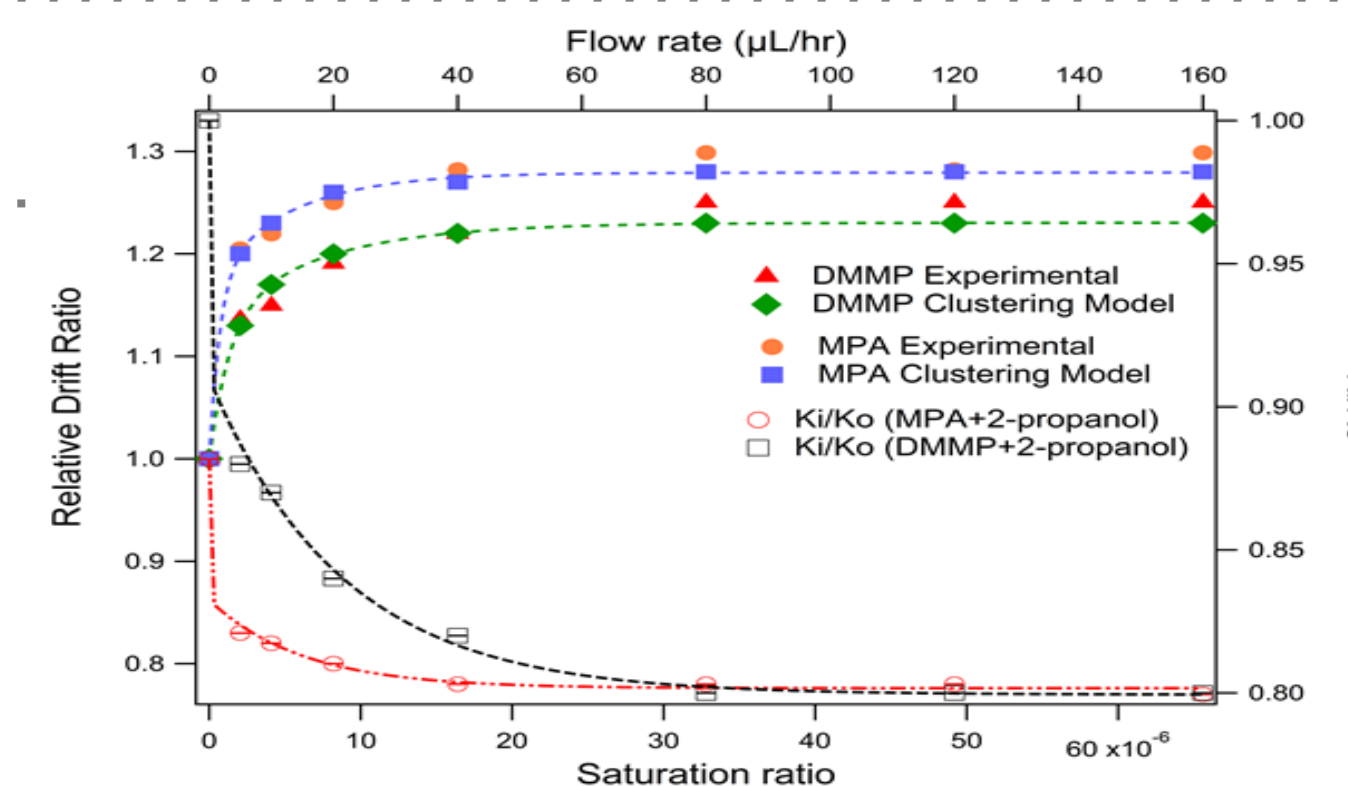


Figure 6. A plot of model comparison of DMMP and MPA against saturation. Reasonable agreement is achieved using the probabilistic model. Saturation ratio is related to flow rate. Comparison of the observed reduced mobility with and without the modifier.

$$\frac{K_{obs}}{K_0} = \frac{1 + \frac{K_1}{K_0} \text{Sexp}\left(-\frac{\Delta G}{kT}\right)}{1 + \text{Sexp}\left(-\frac{\Delta G}{kT}\right)} = \frac{\Omega_0 \mu_1^{1/2}}{\Omega_1 \mu_0^{1/2}}$$

ANALYTE ION	Experimental CCS	Theoretical CCS	Reduced Mass (Da)
[MPA+H] ⁺	91.80 +/- 0.07	91.79	21.73
[MPA+2-PROPANOL+H] ⁺	119.12 +/- 0.19	123.57	23.76
[DMMP+H] ⁺	89.10 +/- 0.07	95.05	22.88
[DMMP+2-PROPANOL+H] ⁺	112.21 +/- 0.26	121.48	24.32

Table 1. A summary of the measured and calculated collision cross section, as well as the reduced masses in (Nitrogen) of the ions

CONCLUSIONS

- Drift gas modifiers induce mobility shifts of up to 20% for the systems probed.
- Species that remain unresolved under normal conditions become fully resolved using drift gas modifiers.
- Systematic assessment of mobility shifts as a function of drift gas modifier concentrations demonstrates selective interactions exist and may be exploited to adjust separation factors

FUTURE DIRECTIONS

- Integrate cluster models to inform mechanisms of interaction between different functional groups.
- Systematically vary the drift gas modifier to develop a predictive capacity.
- Evaluate the impact of temperature on complex stability.
- Extend the approach to more complex mixtures.

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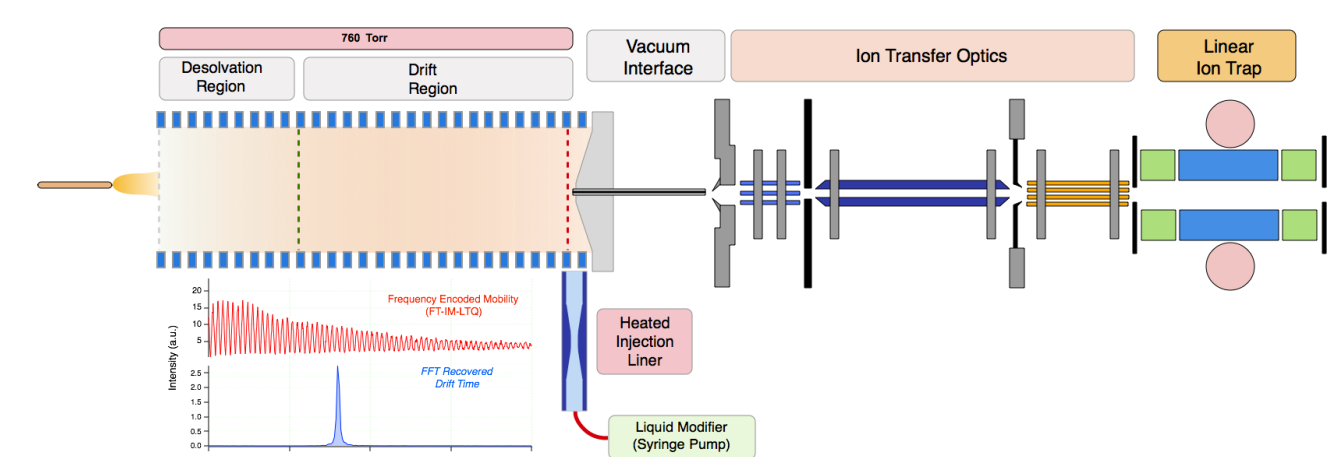


Figure 1. Schematic representation of the atmospheric pressure dual gate ion mobility system coupled with a LTQ mass spectrometer. Mobility spectra may be acquired using either the integrated Faraday plate or by encoding the mobility data in the frequency domain. For the latter the FFT may be used to identify the mobility distributions of m/z selected ion populations. Drift gas modifiers are introduced into the counter-current drift gas using a syringe pump and a temperature controlled heated injection liner.

