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Solvent vapor effects in planar high-field asymmetric waveform ion mobility spectrometry: Solvent trends and temperature effects

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ABSTRACT

Solvent vapor added to the drift gas in a planar high-field asymmetric waveform ion mobility spectrometer (FAIMS) leads to dramatic shifts to larger CV values while retaining narrow peaks, leading to dramatically increased resolving power (up to ~140) for a variety of ions including isomeric ions. Here we present studies designed to improve the fundamental understanding of the role of solvent vapor on performance of planar FAIMS, focusing on solvent trends with molecular size and effects of temperature. The studies employ as test compounds the $[M-H]^-$ ions of the three positional isomers of phthalic acid and the M^- and $[M-H]^-$ ions of trinitrotoluene (TNT). The addition of solvent vapor to FAIMS carrier gas has a significant impact on the behavior of the ions inside the FAIMS cell and can impact the overall performance of the cell. We have shown that by comparing a range of solvent vapors (water and C_1–C_4 alcohols), the magnitude of the effect correlates to the molecular volume of the solvent molecule. This fits well with the model of clustering/declustering of ions with neutral molecules on the time scale of waveform used in FAIMS. We have also shown that with the addition of heat, the effect of the solvent vapor is lessened, as one would expect with the cluster/decluster model.

1. Introduction

High-field asymmetric waveform ion mobility spectrometry (FAIMS) separates and filters ions generated by various atmospheric-pressure ionization methods [1,2]. The major difference between FAIMS and conventional ion mobility spectrometry (IMS) is the magnitude of and method of applying the electric field. In conventional drift-tube IMS at ambient pressure, a constant electric field, generally less than 200 V/cm, is applied parallel to the direction of separation, and is used to move the ions from the entrance to the exit of the drift tube. In FAIMS, a much higher electric field, generally greater than 10,000 V/cm, is applied perpendicular to the direction of separation, while the drift gas is used to move the ions in the direction of separation. Furthermore, the electric field in FAIMS is not constant, with an asymmetric waveform alternating between periods of opposite polarity.

The principles of operation of FAIMS were first described by Buryakov et al. [3], and further detailed by Guevremont et al. [2,4,5]. Ions that are subjected to an electric field in a drift gas will move along the applied field lines with a velocity given by the following equation:

$$v = K \times E \tag{1}$$

where v is the drift velocity of the ion, K is the coefficient of ion mobility, and E is the applied electric field strength. At low electric fields at ambient pressure, ~200 V/cm, K is independent of applied electric field and ions with different K values travel at different velocities [3,6].

At the higher electric fields used in FAIMS, >~10,000 V/cm, K becomes dependent on applied field strength in a non-linear manner [3]. The high-field mobility is referred to K_h, a high-field mobility term that varies depending on field strength. The dependence of mobility at high-field can be described by the following equation:

$$K_h = K\left[1 + \alpha\left[\frac{E}{N}\right]^2 + \beta\left[\frac{E}{N}\right]^4 + \cdots\right] \tag{2}$$

where K_h is the high-field mobility, K is the low-field mobility, E is the applied electric field in V/cm, N is the gas number density in molecules/cm^3, and α and β are ion-specific dependencies on applied electric field (i.e., the $[M+H]^+$ and M^+ ions may have different α and β) [4].

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To generate the high fields used in FAIMS, a radio frequency (RF) asymmetric waveform is typically applied to one plate while the other plate is held at or near ground. This asymmetric waveform, $V(t)$, is composed of a high-voltage portion, often referred to as dispersion voltage (DV, 0 to peak) applied for a short period of time (V_1 and t_1) and a lower voltage, opposite-polarity portion applied for a longer period of time (V_2 and t_2). The sum of the time-voltage products of the waveform is equal to zero, as shown in the following equation [2–4]:

$$V_1 \times t_1 + V_2 \times t_2 = 0 \tag{3}$$

As a result of the high-field dependence on ion mobility, ions will experience two different mobilities during one cycle of the asymmetric RF waveform, which generates two different velocities (Eq. (1)). As ions move through the cell perpendicular to the applied field, they will experience a net displacement toward one of the electrodes if there is a difference between the two velocities. If an ion experiences enough cycles of the asymmetric waveform, it will strike one of the two electrodes and be neutralized. To offset an ion's net displacement, a small direct current (DC) potential is applied to one of the electrodes and is referred to as a compensation voltage (CV). This CV value is essentially a measure of the difference in mobility of an ion at the two different applied fields. Since K_h is ion-dependent, the magnitude of the CV needed to offset the net displacement can be different for different ions, including isomeric ions [7–9]. Under the conditions appropriate to transmit one ion, i.e., correct DV and CV, other ions will drift toward one of the plates and be lost. FAIMS spectrometers essentially act as ion filters which selectively transmit ions with the appropriate ratio of K_h to K. A mixture of compounds can be analyzed by scanning the CV over a range of voltages, producing a CV spectrum. The CV can also be held constant, allowing specific ions to be transmitted [1,3,4].

In general, FAIMS spectrometers are composed of two plates, planar or curved, placed a uniform distance apart. Planar geometries typically offer higher specificity and resolving power at a cost of lower transmission [10], whereas curved geometries offer greater transmission due to an electrostatic focusing effect at a cost of lower resolving power [5,11]. Resolving power for a FAIMS spectrometer is defined by the following equation:

$$R_p = \frac{\left|\mathrm{CV}\right|}{\mathrm{FWHM}} \tag{4}$$

where R_p is the resolving power, $|\mathrm{CV}|$ is the absolute value of the measured compensation voltage for a particular ion, and FWHM is the full width in volts at half maximum height for the CV peak. Resolving power is an instrumental parameter that estimates how well the instrument (and conditions under which it is operating) can separate or resolve two ions with similar behaviors [12]. The resolution between two specific peaks is defined by the following equation:

$$R_s = \frac{\left|\mathrm{CV}_2 - \mathrm{CV}_1\right| \times 2}{\left[\mathrm{PW}_{2_{10\%}} + \mathrm{PW}_{1_{10\%}}\right]} \tag{5}$$

where R_s is the resolution, CV_1 and CV_2 are the CV values for the ions of interest, and $\mathrm{PW}_{2_{10\%}}$ and $\mathrm{PW}_{1_{10\%}}$ are the peak widths in volts at ten percent of the full height.

As shown in Eq. (2) above, the dependence of K_h on high-field depends on two ion-specific terms, α and β. Of particular interest to us is how ion chemistry can affect those terms, and therefore the way ions behave in the FAIMS spectrometer. Previous work has shown that when water vapor concentrations or contamination in the drift gas is high, there are very apparent chemical effects [4,13–16]. When water or other vapors are present in the carrier gas, an ion may collide with those neutral molecules and form complexes or clusters. These complexes in turn may have different mobilities at the two different fields used in FAIMS as compared to the bare ion. In FAIMS spectrometers using curved plates, these complexed ions will not be efficiently resolved, or may be lost altogether from the FAIMS spectrometer due to the focusing effect [4,5,11]. Indeed, it is widely considered to be critical that dry gases be used with curved plate geometry. Otherwise, ion CV peaks are observed to broaden and signal is lost altogether [2,13]. Due to this generally accepted need for dry gas in curved plate FAIMS spectrometers, it has been shown that careful selection of ionization and injection conditions at the entrance of the FAIMS spectrometer is important for good performance. Particularly important are the flow rate of the solution into the ionization source, the flow rate of the drift gas and the solvent composition of the analyte solution [13].

Eiceman and coworkers showed that concentrations of water in the drift gas above approximately 50 ppm caused CV shifts of organophosphorus ions using a micromachined planar FAIMS spectrometer [15]. These shifts were explained by a formation of water–ion complexes during the lower voltage portion of the asymmetric waveform which were dissociated to bare ions during the higher voltage portion of the waveform. The complexation of the ions was enough to change their mobility so that the difference between the lower field mobility and higher field mobility changed [14,17]. This group also reported the addition of dopant compounds to the carrier gas to assist in the detection of explosives [16]. Other groups have shown separation of the isomers of phthalic acid by the addition of carbon dioxide to the carrier gas [8,18].

Much of the work exploring the effects of solvent vapors or contaminants has concentrated on either curved FAIMS spectrometers coupled with mass spectrometry or micromachined planar FAIMS spectrometers. Both of these geometries offer some interesting insights into the effects of solvent vapor on performance of the FAIMS spectrometer. For curved geometries, detailed investigations into solvent vapor effects using high concentrations were thought not possible, as the focusing effect would cause a dramatic decrease in ion signal or a complete loss of ion signal all together [4,13,14]. Recent work has however shown some benefits to the addition of solvent vapor to the carrier gas in curved geometries [28]. Ion signal in a micromachined planar geometry FAIMS spectrometer is not as affected by solvent vapor due to the lack of ion focusing effect. Micromachined geometries, however, do not offer very high resolving powers due to the small size and short ion residence time. It has been shown that the resolving power of a FAIMS spectrometer, particularly planar geometries, increases as the residence time inside the cell increases [19,20]. Increasing the residence time inside the cell does, however, have the potential side effect of lowering the sensitivity of the instrument due to increased diffusional losses. Higher resolving power planar FAIMS cells have been built by Smith and coworkers, showing resolving powers up to at least 40 [20]. Recently published work from this research group focused on initial investigations into solvent vapor effects on FAIMS ion behavior using the aforementioned higher resolving power FAIMS cells [21], demonstrating resolving powers up to 140. Similar solvent effects studies and applications have been reported by others [29,30].

The work presented here is aimed at improving the fundamental understanding of the role of solvent vapor on performance characteristics of planar FAIMS. The two main areas of focus: solvent trends and temperature effects, help to better characterize the effects of solvent vapor in planar FAIMS and lead to potential extensions of the technique as a whole.