Evaporation and Discharge Dynamics of Highly Charged Droplets of Heptane, Octane, and \( p \)-Xylene Generated by Electrospray Ionization

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We report studies of the evaporation and discharge dynamics of highly charged droplets generated by electrospray ionization from \( n \)-heptane, \( n \)-octane, and \( p \)-xylene doped with Stadis-450, a conductivity-enhancing agent. A phase Doppler anemometer (PDA) characterizes individual droplets moving through the uniform electric field within an ion mobility cell according to size, velocity, and charge. Repeated reversal of the electric field allows multiple PDA measurements on selected droplets with diameters ranging from 3 to 60 \( \mu \)m and up to \( 10^7 \) elementary positive charges. This “ping-pong” technique provides individual droplet histories from which we determine the dynamics of solvent evaporation and charge loss. On average, \( n \)-heptane discharges at 101% of the Rayleigh limit of charge, while \( n \)-octane and \( p \)-xylene droplets discharge at 87% and 89% of their respective limits. Discharge events release an average of 19% of the charge in \( n \)-heptane and 17% of the charge in both \( n \)-octane and \( p \)-xylene. Within the limits of the measurements, no detectable change in droplet diameter accompanies observed discharge events, indicating the loss of a relatively small fraction of the total volume. We compare these results to previous experiments, theoretical models for droplet evaporation and discharge, and predictions from the Rayleigh model. We report both Stadis-450 and triethylamine mass spectra in octane and discuss issues regarding the use of hydrocarbon solvents in electrospray mass spectrometry.

Despite the widespread use of electrospray ionization as a popular technique in mass spectrometry, questions remain regarding the processes leading to the formation of desolvated ions seen in mass spectra.\(^1,2\) Lord Rayleigh developed critical theories of charged droplets, balancing the forces of surface tension and charge repulsion to determine charged droplet stability.\(^3\) His work suggests that, in a droplet of radius \( r \) and surface tension \( \gamma \) in a medium of electrical permittivity \( \varepsilon \), charge repulsion will overcome surface tension at a charge \( q_{\text{cr}} \) given by eq 1. When this condition is met, Rayleigh predicts that droplets undergo a disruptive event in which “the liquid is thrown out in fine jets, whose fineness, however, has a limit”. Although this suggests a mechanism for the discharge event, his model lacks a quantitative description of the charge loss or specific relationships between the progeny drop or droplets and the parent.

The application of electrospray to mass spectrometry by Yamashita and Fenn renewed an interest in charged droplet breakup.\(^4\) Recent articles by Cole\(^5\) and Kieberl\(^1\) summarize the research performed to elucidate the dynamics not described by Rayleigh’s analysis. In the consensus view, droplets in the micrometer size regime eject numerous progeny droplets having a diameter roughly one-tenth that of the parent. We refer to this event as a Rayleigh discharge, or simply discharge, rather than the more common term, fission, which has other connotations. Other experiments and models such as the ion desorption model\(^6-8\) and the charge residue model\(^9,10\) address phenomena involving smaller droplets in the nanometer regime and are not considered in this study. Charged droplets have been observed to undergo Rayleigh discharge while they are only at 70%–90% of their Rayleigh limit. For instance, Taflin and co-workers found discharge occurring below 90% of the Rayleigh limit with charge loss ranging from 10% to 18% and 1%–2% mass loss in dodecanol, hexadecane, heptadecane, dibromo octane, and bromocyclo.\(^11\) These results for low-vapor pressure organic solvents are quoted widely. More recently, Duft and co-workers\(^12\) explored Rayleigh discharge through accurate measurements of the quadrupole oscillations in a droplet suspended in an alternating current electric field. Through a calculation of the Coulomb energy and surface energy of a droplet they determined that ethylene glycol undergoes discharge at its Rayleigh limit. Recent studies in our laboratory focused on the more common electrospray solvents water, methanol, and acetonitrile. This work suggests a solvent dependence on the charge loss and the percent Rayleigh limit at discharge.\(^13,14\) These results are summarized in Table 1.

\[ q_{\text{cr}} = 8\pi r^2 \varepsilon_{\text{d}} \varepsilon_0^2 \varepsilon_{\text{d}}^2 \gamma^2 \]  

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\(^3\) Rayleigh, L. Philos. Mag. 1882, 14, 184–186.


Table 1. Physical Parameters and Experimental Charge Loss Values for Solvents Characterized by the “Ping-Pong” Technique

<table>
<thead>
<tr>
<th>solvent</th>
<th>dielectric constant, $\epsilon$</th>
<th>surface tension, $\gamma$ (mN m$^{-1}$)</th>
<th>%charge loss</th>
<th>%Rayleigh limit</th>
<th>evaporation temp, $T_e$ (K)</th>
<th>slope, $s$ (\mu m$^2$ s$^{-1}$)</th>
<th>theor</th>
<th>exptl</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrile</td>
<td>36.64</td>
<td>28.66</td>
<td>15–20</td>
<td>120</td>
<td>270</td>
<td>$-6500$</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>methanol</td>
<td>33.0</td>
<td>22.07</td>
<td>15–20</td>
<td>120</td>
<td>267</td>
<td>$-4750$</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>water</td>
<td>74.6</td>
<td>71.99</td>
<td>20–40</td>
<td>100</td>
<td>270</td>
<td>$-1250$</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>n-heptane</td>
<td>1.921</td>
<td>19.65</td>
<td>19 (6)</td>
<td>101 (4)</td>
<td>278</td>
<td>$-11900$</td>
<td>11000</td>
<td>11000</td>
</tr>
<tr>
<td>n-octane</td>
<td>1.944</td>
<td>21.14</td>
<td>17 (10)</td>
<td>87 (8)</td>
<td>287</td>
<td>$-3670$</td>
<td>4900</td>
<td>4900</td>
</tr>
<tr>
<td>p-xylene</td>
<td>2.274</td>
<td>28.01</td>
<td>17 (6)</td>
<td>89 (3)</td>
<td>289</td>
<td>$-2200$</td>
<td>2400</td>
<td>2400</td>
</tr>
</tbody>
</table>

Values in parentheses are standard deviations. Acetonitrile, methanol, and water data are taken from Smith and co-workers. Physical constants at 293 K are taken from Lide. Theoretical evaporation parameters are calculated from eqs 2–4. n/a, not available.

Fernandez de la Mora approached the question of solvent dependence in droplet discharge phenomena by a comparison to the dynamics of a cone-jet at an electrospray needle. The critical voltage for the onset of electrospray increases with surface tension while solution conductivity influences spray current and viscosity affects initial droplet size. Accordingly, he proposed that the flow of charge (e.g., current) through the discharge event is proportional to the surface tension while the flow of solvent is proportional to both the surface tension and the dielectric constant of the solvent. Additionally, low-conductivity solutions discharge mass and charge through large cones relative to their more conductive, polar counterparts. A corresponding treatment for low-conductivity solvents is not as well developed, but correlations between a solvent’s experimental discharge characteristics and its physical properties may still be explored. Such explorations motivate the current investigation.

Polar liquids are the primary solvents for electrospray ionization, and their discharge dynamics have been well studied. On the other hand, high-volatility hydrocarbons and similar low-conductivity solvents are not widely employed for electrospray mass spectrometry and their Rayleigh discharge characteristics have received less attention than more commonly used polar solvents such as water and methanol. Several researchers present spectra of crude oils and hydrocarbon fuels dissolved in solutions of polar solvents. Rebek and co-workers reported the use of benzene and xylene without the addition of polar solvents, but few others routinely employ hydrocarbons as solvents for analytical applications of electrospray mass spectrometry. Tang and Gomez generated a stable electrospray of n-heptane, focusing on the dynamics of the spray itself, as well as size determinations and percent Rayleigh limit approximations for droplets within the spray. M ost recently Leisner and co-workers have developed experimental methodologies for studying the evaporation and discharge dynamics of low-volatility solvents. They have acquired images of a discharge event from glycerol characterized by simultaneous, symmetrical emission of two fine streams of progeny droplets from opposite sides of the droplet. This contrasts with the previous work of both Gomez and Tang, as well as Kebarle and co-workers, who presented visual evidence of droplet distortions leading to discharge from a single point on a parent droplet near the Rayleigh limit for heptane and methanol, respectively.

We report the evaporation and discharge dynamics of three volatile hydrocarbon solvents and relate the dynamics to previously researched solvents widely employed in electrospray mass spectrometry. The present work investigates positively charged 3–60 nL droplets of n-heptane, n-octane, and p-xylene with up to 10$^7$ elementary charges. To reduce droplet sizes to a range accessible for measurement using our experimental methodology, Stadis-450, a conductivity-enhancing agent, is added to each of these solvents. Previous studies demonstrated that Stadis-450 does not significantly affect the surface tension and the dielectric constant of bulk heptane in concentrations up to 3%.

Discharges are characterized by measuring the droplet diameter and charge, as well as the charge loss at the time of the event. We are not able to detect mass loss associated with a discharge event. Overall mass loss due to evaporation is measured and compared against models. Equations 2 and 3 model the evaporation of droplets larger than 1.0 $\mu$m in diameter following a notation consistent with Hinds. Here $d_0$ refers to the droplet diameter as a function of the initial droplet diameter, $d_0$, time $t$, and solvent parameters in $s$, defined in eq 3. Solvent parameters include $D_p$. 

\begin{align*}
\text{d}_p^2 &= \text{d}_o^2 + \text{st} \\
\text{s} &= -\frac{8D_p(T_p)M}{R_p(T_p)} \frac{P_p(T_p)}{T_p}
\end{align*}

References:


The diffusivity of solvent vapor in gas $j$, solvent molar mass $M$, droplet density $\rho_d$, and equilibrium vapor pressure, $p_v(T_p)$, at equilibrium surface temperature $T_p$, while $R$ is the gas constant. Equations 2 and 3 are simplified from more rigorous models in which solvent vapor in the ambient gas inhibits evaporation. Experimentally, a constant flow of dry nitrogen gas through the apparatus flushes solvent vapor, allowing for this simplification. Spontaneous evaporation is endothermic, lowering the surface temperature to a size-independent equilibrium value, $T_p$, given by eq 4. $T_p$ is determined by the ambient gas temperature, $T_\infty$, and

$$T_p = T_\infty - \frac{D_j(T_p)\Delta H_vap(T_p)\rho_v(T_p)}{Rk_v(T_p)}$$

thermodynamic values $\Delta H_vap(T_p)$ and $k_v$, the heat of vaporization and the thermal conductivity of the medium, respectively. Equation 4 must be iteratively solved for the equilibrium temperature because several parameters are temperature dependent. Heat of vaporization and vapor pressure data from Yaws$^{28}$ and diffusivity data from Vargaftik et al.$^{29}$ are inserted into eqs 3 and 4 for the evaporation of the three solvents in the present study, as well as for methanol, acetonitrile, and water for comparison with previous studies.$^{14}$ The diffusivity for p-xylene was approximated by using the value for toluene. Table 1 lists the calculated solvent parameters, $s$, for the evaporation of acetonitrile, methanol, water, heptane, octane, and p-xylene.

We additionally present data illustrating the use of these hydrocarbon solvents in conventional electrospray mass spectrometry analyses. Spectra are reported for both Stadis-450 and triethylamine in octane.

**EXPERIMENTAL SECTION**

The experimental setup is shown in Figure 1. The hardware, experimental procedures, and methods of data analysis are discussed in detail elsewhere.$^{11,14}$ Droplets are produced at the electrospray ionization source and directed upward through the ion mobility spectrometer (IMS) drift cell for analysis. A polished hypodermic stainless steel needle (R-HTX-35, 64-μm i.d., 150-μm o.d., Small Parts, Inc.) mounted on a three-dimensional stage sprays upward through two sequential apertures on the bottom of the drift cell. The first aperture is 500 μm in diameter and biased at +100 V. One centimeter above the first, the second aperture is 1.5 mm in diameter and maintained at earth ground. To generate positively charged droplets between 10 and 60 μm in diameter, the electrospray needle is biased between +800 and +1200 V, solutions are driven at rates between 0.2 and 1 μL min$^{-1}$, and the distance between the hypodermic needle tip and the first aperture is adjusted between 0.5 and 5 mm. Our experimental arrangement selects droplets close to the axis of the spray.

Eight vertically stacked, resistively coupled, stainless steel rings define a 20-cm-long, 4-cm-inner diameter drift region within the IMS. Dry nitrogen gas at ambient temperature (293 K) flows downward through the drift cell to ensure the droplets are evaporating in an environment free from solvent vapor. In the center of the cell, ~10 cm above the electrospray source, two intersecting HeNe laser beams form the measurement volume, roughly 150 μm in diameter, of the phase Doppler anemometer. The phase Doppler anemometer acquires the velocity, $v_\parallel$, and diameter, $d_\parallel$, of the droplet. These values yield the net droplet charge, $q$, through the force balance eq 5, which applies to droplets larger than 1 μm in diameter.$^{10,11}$ Here $m_0$ is the mass of the particle; $C_0$, $C_D$, and $\rho_{air}$ are the atmospheric slip correction factor, drag coefficient, and density of air, respectively, $E$ is the magnitude of the electric field, and $g$ is the force of gravity. The slip correction and drag coefficient are calculated from Seinfeld and Pandis.$^{30}$ Equation 5 depends on the direction of the electric field vector relative to the force of gravity. The gravitational term is added to or subtracted from the velocity term corresponding to the direction of the electric field, either antiparallel or parallel to gravity, respectively.

**Ping-Pong Technique.** A 50.6 V cm$^{-1}$ electric field initially directs positively charged droplets upward through the cell. Droplets initially travel at ~50 cm s$^{-1}$ taking ~200 ms to reach the measurement volume. Data used to determine droplet size and velocity are acquired by the PDA and recorded using a digital oscilloscope when a droplet drifts through the measurement volume. The oscilloscope triggers two high-voltage MOSFET switches (MTP1N100E, Motorola) that reverse the cell voltages.

![Figure 1. Experimental apparatus for studying droplet evaporation and discharge dynamics. Droplets are generated by the electrospray source and directed through two apertures into the drift region of the ion mobility cell. Droplet “ping-pong” commences when a droplet passes through the measurement volume of the PDA.](image)


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causing the droplet to travel downward through the measurement volume. This switching repeats and the droplet ping-pongs through the measurement volume until it is no longer detected, either because of evaporation to an undetectable size or from drifting beyond the measurement volume. The latter is the principle reason for terminating acquisition, as no radial trapping force exists in the cell. The result is a history of the droplet's diameter, velocity, and charge sampled every 10 ms.

**Experimental Conditions.** Solvents n-heptane (99.5% Mallinckrodt), n-octane (97% GC grade, Alfa-Aesar), and p-xylene (99+ % HPLC grade, Aldrich) were used without further purification. The conductivity enhancer, Stadis-450 (Octel America), was added in 1 vol% to n-heptane and n-octane and 0.1% to p-xylene. The electrospray needle was held 2 mm away from the first aperture of the IMS, maintained at 875 V for n-heptane and n-octane, and maintained at 1060 V for p-xylene. In each case, solution flow rates were 0.2–0.5 mL min⁻¹ and dry nitrogen gas flowed downward through the cell at 0.3 L min⁻¹ or 0.6 cm s⁻¹.

**Electrospray Ionization Mass Spectrometry.** A Finnigan LCQ ion trap quadrupole mass spectrometer acquired the mass spectra. A custom-built source using a fused-silica nanospray needle (New Objective, 15-µm-i.d. tip) replaced the standard electrospray ion source. During acquisition, the capillary was not heated, and the sheath gas was removed. The signal was optimized using the built-in tuning capabilities of the LCQ. Triethylamine (99.5% Aldrich) was used without further purification.

**RESULTS**

Representative data for a single droplet of p-xylene are shown in Figure 2. Large, simultaneous decreases in velocity and charge signal the occurrence of discharge events, as indicated by arrows. Specifically, plot a shows constant evaporation and a steadily decreasing diameter. Initially, constant charge and decreasing mass leads to an increase in the velocity (b) as the electric force, \( qE \), steadily becomes stronger relative to the force of gravity, \( m_p g \). The small oscillations in velocity correspond to motion with and against gravity. As a result of constant charge (c) and steadily decreasing mass, the droplet approaches its Rayleigh limit (d). This trend continues for the first 0.14 s of the droplet data acquisition at which point the velocity, charge, and percent Rayleigh limit (100 \( q/q_R \)-1) decrease dramatically. The sudden decrease in droplet charge results in a similarly large decrease in velocity, as the change in \( qE \) is significantly larger than the change in \( m_p g \). We interpret this rapid loss of charge to be a Rayleigh discharge event.

Table 1 summarizes the discharge and evaporation characteristics of the three solvents studied along with the corresponding data for acetonitrile, water, and methanol previously reported from our laboratory. Between discharge events, individual charge values are averaged, which is illustrated by the dotted lines in Figure 2c. Percent charge loss is determined from the difference between the average charge levels before and after a discharge event. The percent Rayleigh limit at discharge is simply the last recorded value before the sharp decrease characteristic of a discharge event. Both the percent charge lost and the percent Rayleigh limit data are explored with histograms for each solvent in Figure 3a and b, respectively. As the distribution of each is roughly Gaussian in shape, Table 1 lists standard deviations for these data in parentheses. A linear regression of diameter squared versus time generates the parameters that quantify evaporation. Figure 4 shows an example of the fitting performed on the diameter measurements from Figure 2a. The resulting slope values are averaged in Table 1 for each solvent. Note that this treatment ignores diameter decreases that result from discharge events.

Both n-octane and p-xylene were often characterized through 30–50 reversals of the electric field. Up to seven discharge events...
were observed for n-octane, while p-xylene demonstrated up to eight. For example, the acquisition shown in Figure 2 contains five well-defined discharge events highlighted by arrows. Heptane rarely exhibited multiple discharges because its higher evaporation rate results in a shorter residence time in the IMS. Size–charge correlations for droplets from these solvents are shown together in Figure 5. The data represent the diameter versus charge for each droplet immediately preceding its first recorded discharge event.

Figure 6 shows two mass spectra using n-octane as the electrospray solvent. Spectrum a is the averaged mass spectrum showing that a complex array of ions is present when Stadis-450 is added to n-octane. Spectrum b exhibits the ions observed when triethylamine is added to neat n-octane.

DISCUSSION

Size–Charge Distributions. Plots in Figure 5 show typical diameters of 35–45 μm for heptane (a), 35–60 μm for octane (b), and 10–40 μm for p-xylene (c). The droplets in the present study are larger than those produced by common nanospray techniques but are comparable to the sizes employed in other studies of Rayleigh discharge.11,24,31 In plotting points immediately preceding the first recorded discharge event for each droplet, Figure 5 explores the point at which droplets discharge relative to the Rayleigh limit. Size–charge distributions for latter discharge events resemble those shown in Figure 5 and show no additional patterns of interest. Size versus charge does not scale with the Rayleigh limit curves for either heptane or octane as shown on plots a and b, respectively. In both cases, smaller droplets discharge at a higher percent Rayleigh limit than the larger droplets studied. In contrast, p-xylene discharges scale with the Rayleigh limit over the size range studied. The distributions in Figure 5 support the broader standard deviation in the percent

Rayleigh limit at the point of discharge for n-octane and the smaller deviation for n-heptane and p-xylene listed in Table 1 and shown by the histograms in Figure 3.

**Evaporation and Discharge Dynamics.** The average charge loss in a discharge event for all three solvents is 18% ± 1%. This corresponds favorably with studies by Taflin and co-workers, who reported highly accurate measurements on 12 discharge events of low-volatility oils.11 Our data for over 2000 discharge events indicated by arrows. The 4% experimental error in our diameter measurement is significantly larger than the discharge events. No observable discrete decrease in diameter accompanies the discharge events indicated by arrows. The 4% experimental error in our diameter measurement is significantly larger than that of Taflin and co-workers, who reported droplet radii between 10 and 20 μm to within 1 nm.11 Their observed 2% mass loss would correspond to a 0.7% change in diameter, which is significantly below the resolution of our PDA. Therefore, we are only able to put an upper bound on the change in diameter at 4% corresponding to the experimental error in our measurements.

**Successive Discharges.** Earlier “ping-pong” studies in our laboratory revealed up to five discharge events from a single parent droplet in experiments with methanol.14 The electric field generated in the IMS is radially uniform and time-independent transverse to droplet motion along the axis of the instrument. This method contrasts with electodynamic balance experiments, which suspend individual droplets with time-dependent axial and radial fields.32 To observe multiple discharge events from the same droplet in the IMS, the droplet must not drift radially beyond the 150-μm diameter of the PDA measurement volume. Radial momentum is either a result of a droplet’s original path or from another force imparted on it during its residence time in the IMS. The observation of multiple discharges implies that the net position of the droplet is not significantly affected by a discharge event. On this assumption, Smith discussed the implications for the maximum impulse imparted to the parent droplet.13 However, recent observations from Leisner and co-workers of simultaneous emission of two progeny droplet streams in opposite directions would be expected to impart little, if any, momentum to the parent droplet.25 The decreasing time between successive discharges is consistent with the theoretical treatment by Tang and Smith in which the time between discharges is a function of droplet diameter.33 Indeed, since q.R is proportional to ρ.R from the electrical conductivity, 1 and ρ decreases linearly in time from eq 2, it comes as no surprise that the time between events is decreasing. Beyond the five discharges in Figure 2, events occur faster than the 100 Hz data acquisition rate of the experiment. This leads to the observed steady decrease in velocity, as well as the unreliable charge and percent Rayleigh limit information evident in the later period of the acquisition. Further analysis of the multiple discharges in n-octane and p-xylene reveals that, within experimental error, there is no change in the percent charge lost in successive discharge events.

**Comparison of Discharge Characteristics with Polar Solvents.** The data in Table 1 for the six solvents studied with the “ping-pong” experiment suggest a correlation between the percent charge lost and both the dielectric constant, ɛ, and the surface tension, γ, of the solvent. This compares favorably with Fernandez de la Mora’s predictions for charge and solvent flow through a discharge event.15 We assume the electrical conductivity of 4.1 × 10⁻⁸ S cm⁻¹ measured by Tang and Gomez for 1.2% Stadis-450 in n-heptane represents a maximum conductivity for the solutions in the present study. Consequently, there is no correspondence between the discharge characteristics and solution conductivity, which would be significantly higher for the methanol solutions. Previous work in our laboratory found no significant change in the percent charge lost in a discharge event in methanol solutions with varying concentrations of sodium chloride.14 This suggests percent charge loss is also dependent on factors not yet explored.

**Application to Electrospray Mass Spectrometry.** While enhancing the conductivity, Stadis-450 is not a desirable additive for electrospray ionization using hydrocarbon solvents. Figure 6a shows the mass spectrum of Stadis-450 (1 vol %) in octane. The complex distribution illustrated may be difficult to separate from that of an analyte. The spectrum of Stadis-450 is characterized by two pairs of overlapping distributions with peaks separated by 28 m/z, indicating the presence of a polymer with a distribution of polymer chain lengths. Triethylamine was sprayed in octane in a separate experiment without the Statis-450 additive. In positive ion mode, protonated triethylamine appears at 102 m/z. The process leading to protonation of the amine in octane was not

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Figure 6. Mass spectra of (a) Stadis-450 and (b) triethylamine in octane. Stadis-450 is characterized by two pairs of overlapping distributions centered on 382, 536, 1252, and 1378 m/z. Peaks separated by 28 m/z units within each distribution are indicative of a hydrocarbon polymer. The protonated triethylamine spectrum (b) shows contaminants at 118 and 130 m/z.
investigated and may have involved trace impurities as the charge carriers in the droplet.

CONCLUSIONS

Heptane, octane, and p-xylene have discharge characteristics similar to those found for both large, low-volatility hydrocarbons and for traditional electrospray solvents. Successive discharge events observed for n-octane and p-xylene demonstrate no significant change in the percent charge lost for both n-octane and p-xylene. Size–charge correlations for heptane and octane show that smaller droplets discharge at a higher percent Rayleigh limit of charge than larger droplets. Over the size range studied, p-xylene discharges at a consistent charge relative to its Rayleigh limit.

The combination of appropriate conductivity and evaporation rates makes these solvents attractive for electrospray mass spectrometry. The introduction of these hydrocarbon solvents may be important for mass spectrometry applications for analytes that do not dissolve easily in other solvents or those already dissolved in a hydrocarbon solvent and not easily extracted into a more traditional electrospray environment. With a complicated spectrum, Stadis-450 is not an appropriate conductivity-enhancing agent as it could interfere with the interpretation of analyte spectra.

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