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STUDY OF THE FORMATION OF TAYLOR CONE IN HIGH-VACUUM ELECTROSPRAY IONIZATION PROCESS

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Бу ишда статик магнетик масс-спектрометрдан фойдаланиб юқори вакуумли электроспрей ионлашишида Тайлор конусининг ҳосил бўлиши тадқиқ қилинган. Содда юқори вакуумли электроспрей ионлашиш манбаси ишлаб чиқилган ва масс-спектрометрга ўрнатилган. Ҳосил бўлаётган зарядли томчиларга эритманинг таркиби, оқим тезлиги, юқори кучланиш ва температуранинг таъсирлари аниқланган.

В работе исследовано образование конуса Тайлора в высоковакуумной электроспрейной ионизации с использованием статического магнитного масс-спектрометра. Разработан простой высоковакуумный электроспрейный ионизационный источник и установлен в масс-спектрометр. Выявлено влияние состава раствора, скорости потока, высокого напряжения и температуры в образование заряженных каплей.

In this work, the formation of the Taylor cone in high-vacuum electrospray ionization using a static magnetic mass-spectrometer was studied. A simple vacuum electrospray ionization source was designed and combined with a mass-spectrometer. The effect of the solution composition, flow rate, high voltage and temperature on the formation of charged liquid droplets was determined at high-vacuum conditions.

I. INTRODUCTION

Electrospray ionization (ESI) has been used as an ionization method for mass spectrometry (MS) for more thirty years.The electrospray of liquid glycerol from a capillary was observed in 1917 [1], and the electrified liquid meniscus, which took the shape of a cone, was theoretically analyzed by Taylor [2]. Dole et al. described that the molecular ions can be liberated from the electrosprayed droplet [3], and the first electrospray ionization mass spectrometry (ESI-MS) was demonstrated by Fenn et al. [4, 5]. Electrospray is a well-known phenomenon producing fine charged droplets through a small capillary due to a high voltage applied between the capillary and a counter electrode. A typical electrospray process is separated into four steps: electrochemical reactions inside the ESI capillary, which produce charges for analyte ionization; generation of charged droplets at the tip of the ESI capillary; shrinking process of the charged droplets via solvent evaporation and repeated fission; gas-phase ion formation from very fine droplets resulting from the shrinking process. The electric field strength at the needle tip with a planar counter-electrode can be approximated as [6-8):

$$E_n = \frac{2V_n}{r_n \ln(4d / r_n)}, \quad (1)$$

where V_n is the applied voltage, r_n is the outer radius of the needle and d is the distance between needle tip and counter-electrode. A typical value of E_n for a successful

electrospray is 10^6–10^7 V/m [6, 8]. If the electric field is strong enough, the force acting on the anions from the electric field is balanced by the surface tension of the solution forming a cone of liquid, called Taylor cone [2], at the needle end.

Using a modified [9, 10] form of the Hendricks equation [8] the electrospray current i_{es} can be approximated as:

$$i_{es} = Hv_f^{\nu}\sigma_s^{n}E_c^{\varepsilon}, \tag{2}$$

where H is a constant depending on the surface tension and the dielectric constant of the solvent, v_f is the flow-rate, σ_s is the specific conductivity and E_c is the electric field from equation (1).

Nowadays, ESI is widely applied in qualitative and quantitative studies of nonvolatile organic compounds, thermally labile inorganic compounds and biomolecules, which are difficult to analyze using electron impact (EI), atmospheric pressure chemical ionization (APCI), atmospheric pressure photoionization (APPI) and other atmospheric ionization methods. ESI [5, 11] generates intact molecular ions, which are used for mass spectrometry [12, 13] ion mobility spectrometry (IMS) [14] or for ion beam deposition methods like soft landing [15, 16].

However, one of the biggest issues of the ESI technique is the large ion loss during transmission from atmospheric pressure to the low-pressure region of the mass analyzer [17, 18]. Most ion loss occurs at the inlet and skimmer of the ESI-MS interface, and therefore, the ion loss should be reduced by moving the ESI source from ambient environment to the sub-ambient pressure inlet chamber. This concept was initially reported as a design called electrodynamic ionization (EHD) by Evan and coworkers [19], and later developed for several applications [20]. In the 1990's, several new designs of ESI sources operating at low pressure emerged [21, 22]. In these initial designs of sub-ambient pressure ESI, the electrospray was operated at pressures much lower than 0.1 Torr, below the suitable pressure (~1 Torr) for electrical breakdown. In addition, a low operating pressure for ESI may degrade the electrospray performance due to the freezing of the solvents during plume expansion, which results in insufficient evaporation.

One potential solution is to implement those conventional atmospheric pressure ionization techniques inside the vacuum chamber. Aksyonov and Williams developed impact desolvation of electrosprayed microdroplets (IDEM), which uses the charged droplets generated by vacuum electrospray [23]. Analytes were dissolved in an electrolyte solution that was electrosprayed in vacuum, producing highly charged micron and submicron-sized droplets. The electrosprayed microdroplets were accelerated by 5–10 kV to velocities of several kilometer per second and allowed to impact a target. The energetic impacts led to desorption of analyte molecules dissolved in the droplets.

In this work, the formation of Taylor cone in high vacuum using a magnetic sector mass-spectrometer MI-1201 was carried out. For this purpose, a handmade vacuum ESI source has been constructed and tested on the magnetic sector mass-spectrometer MI-1201. Specifically, solution was introduced into the vacuum chamber by direct capillary sampling, and simultaneously, a high voltage (HV) was applied onto the ESI emitter. Initial research on the characterization and application of the proposed VESI was demonstrated.

II. EXPERIMENTAL METHODS AND MATERIALS

The developed vacuum electrospray source (VESI) was mounted on a magnetic sector mass-spectrometer, and the scheme of the instrument structure is shown in Fig. 1. A needle with the outer diameter 0.5 mm and inner diameter 0.05 mm was used as an electrospray emitter. The transportation of liquid was directly performed using an ESI emitter. In order to avoid freezing liquid the electrospray emitter was slightly heated using a ceramic cartridge that was embedded of the interface. The temperature of emitter was 60°C in all the experiments. The liquid was pushed to the tip of capillary using a handmade liquid pump with flow rate of 1–10 μl/min.

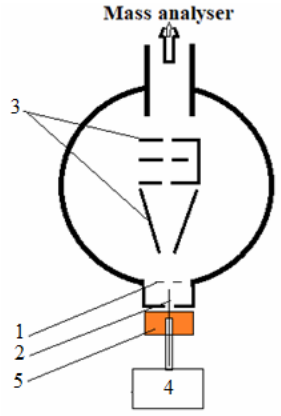


Fig. 1. Scheme of the experimental system: 1 – extracting electrode, 2 – syringe needle (inner diameter 0.05 mm), 3 – focusing lens, 4 – handmade syringe pump, 5 – polyvinylchloride isolator.

All the experiments were conducted using a magnetic sector mass-spectrometer MI-1201. The surface ionization ion source was removed and instead of it the vacuum electrospray ionization source was embedded. The electrosprays are generated inside a vacuum chamber at the pressure 10^{-5} Torr. The charged liquid droplet beam produced from the electrospray emitter was accelerated towards the Faraday cup with an accelerating voltage up to 5 kV.

The charged liquid droplets were generated by electrospraying water and ethanol (1/1) with adding acetic acid of 0.5%. The solution was prepared at different ratios of water and ethanol and the optimal ratio of water to ethanol was also investigated. They were transported into the ion focusing system and accelerated by 5 kV after exiting the ion focusing system. The pure ethanol and water were used in all experiments. Water was purified and deionized by Simplicity UV (Millipore, Bedford, MA, USA).

III. EXPERIMENTAL RESULTS AND DISCUSSION

One of main issue of vacuum ESI (VESI) is to prevent freezing the liquid. The solvent is easy cooled and freezes at the spray tip because of rapid evaporation [24]. Drops freezing can likely occur during the entire electrospray process in vacuum because the solvent will continuously evaporated and cause evaporative cooling. In that case, Coulomb explosion may be terminated that can significantly reduce ionization efficiency. Some related studies have been carried out to produce a stable electrospray under vacuum as well as primary cluster ion source for secondary ion mass spectrometry analysis [25, 26]. Because to prevent ice formation, additional devices, such as a wire heater [27] or a continuous infrared laser [25, 26] were commonly used to heat the liquid.

Ion production from an electrospray source is related to the solution flow rate [28]. In general, liquid transfer rate in a capillary is determined by many factors, including the pressure difference between the two capillary outlets, capillary dimension, and sample viscosity [29]. One feature of the self-aspirating capillary introduction is that the sampling rate is difficult to change during the experiment. This approach helps ensure the

stability of detection for a single measurement. However, the viscosity varied the fofmation of ions, the performance of VESI became dependent on the solution composition. In some cases, the experimental configurations needed to be readjusted for optimization when the sample was changed.

There are the large numbers of solvents that can be used for electrospray ionization under ambient conditions, but there is relatively few suitable for in-vacuum electrospray. We found that ethanol is the most suitable for the electrospray and the stability of the spray in vacuum. The mixture of ethanol and water in various ratios were tested. The solution was continuously sampled through the needle, and a high voltage was directly applied to the emitter. During this sampling process, the pressure of the chamber increased from 1×10^{-6} Pa to 6×10^{-5} Pa. It has been established that the mixture of ethanol and water (75:25 ratio) is also highly suitable for electrospray stability in a vacuum. The dependence of ion current as a function of ratio of ethanol and water is shown in Fig. 2. The applied high voltage to the emitter was 3 kV. As shown in Fig. 2 the maximum ion current of more 4 nA was observed in mixture water and ethanol (ratio 75:25) without applying heat to the electrospray emitter. However, to increase the ethanol amount in mixture further leaded to decrease the ion current.

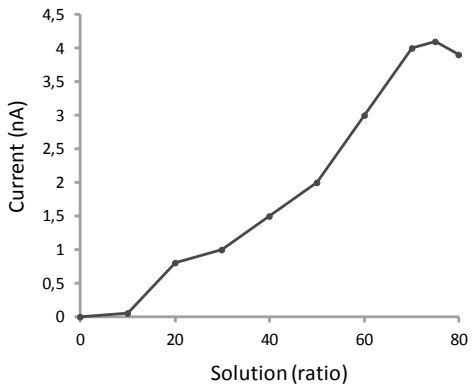


Fig. 2. Ion current as a function of mixture of ethanol and water ratio.

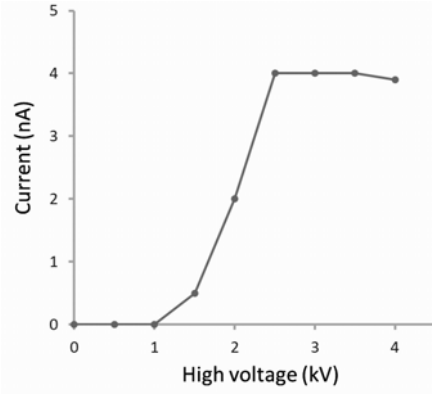


Fig. 3. Ion current as a function of high voltage.

For VESI operation, spray voltage is another indispensable condition. We have studied the influence of the spray voltage on VESI. The mixture of ethanol and water (75:25 ratio) was used for the experiments. Fig. 3 shows the dependence of the electrospray current as a function of high voltage. Electrospray current increased with the applied voltage, and a voltage greater than 1.5 kV was required to operate the VESI. However, the signal disappeared after the high voltage was removed. This observation was consistent with the characteristics of a traditional ESI source. Hence, the detected ions were mainly produced from ESI mechanism.

In order to improve the ionization efficiency, we were also studied the temperature effect on the ion current. For this purpose the mixture of ethanol and water were diluted in a ratio of 50:50. The applied maximum temperature to the electrospray emitter was 60°C because of most organic compounds could be degraded at high temperature. The ion current dependence of charged droplets as a function temperature is depicted in Fig. 4. The curve shows that the ion current increased at the high temperature of the emitter.

The large current of about 4.5 nA was obtained even with a ratio of 50:50 for the mixture of ethanol and water. However, the extraction voltage necessary for stable cone-jet emission is significantly lower for the heated emitter. The total currents registered by the Faraday cup are significantly higher in the heated case. Heating also appears to produce a more divergent spray. These experiments demonstrate that temperature, high voltage and the amount of ethanol in solution play an important role in the formation of stable Taylor cone in VESI.

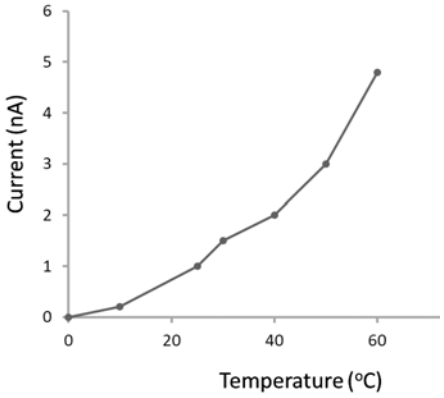


Fig. 4. Ion current as a function of temperature.

IV. CONCLUSION

In this study, the first time VESI using a magnetic sector mass spectrometer MI 1201 was carried out. For the purpose, the extremely simplified VESI source was designed and coupled to the mass spectrometer. The stable Taylor cone was obtained in high vacuum and a large current was obtained even with a rough adjustment. It has been established that the formation of the stable Taylor cone depends on many factors such as flow rate of solution, applied high voltage and temperature of electrospray emitter. The best solution ratio of ethanol and water was 75:25 without applying any heat to the electrospray emitter. However, applying the heat to electrospray emitter at 60°C may increase the formation of charged liquid droplets as well as decrease the ethanol amount in solution. Based on these results, it is concluded that this vacuum electrospray technique has a promising future for analyzing organic compounds such as peptides and narcotics as well as to elucidate their electrospray ionization mechanisms in high vacuum.

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