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Polymer track membranes for atmospheric pressure field extraction of ions from liquid solutions

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ABSTRACT

An approach to the generation of gas phase ions by field extraction from liquid solutions has been investigated. The method uses a polymer membrane with nano-size channels as an interface between the liquid and the atmospheric pressure gas. Ions are produced by dissociation in the polar solvent and secondary ion-molecular reactions in the solution, which fills the channels of the membrane. Field extraction of the ions from the channels is stimulated by pulses of the electric discharge between the membrane and an adjacent electrode in the gas. The gas-phase ions are removed from the extraction zone by air flow and are detected by mass spectrometry. Possibilities of the membrane interface for generation of gas phase ions have been demonstrated from mass spectral investigation curried out for angiotensin II, gramicidin S and cytochrome C solutions. The current kinetics of the membrane ion source has been investigated to elucidate the mechanism of the ion extraction.

1. Introduction

The development of new methods of generating gas phase ions and ion beams is important in various fields of science and engineering. For example, mass spectrometry relies upon the production of ions in the gas phase as a necessary step in any analysis. In particular, biological mass spectrometry needs nondestructive methods for generation of gas phase ions of relatively large, nonvolatile and thermally unstable bioorganic molecules. One widely used method for generating the ions of such molecules from liquid solutions is electrospray ionization (ESI) [1]. In the ESI ion source, the ions are produced by spraying solutions from the tip of a micron-size capillary in the electric field. Using atmospheric pressure conditions, the electrostatic spraying results in generation of gas phase ions that are formed by several consecutive processes. Firstly, multi-charged droplets of micron size are generated. Evaporation of solvent molecules leads to increasing electrostatic repulsion between the charges in each droplet and, eventually, fission of a droplet into two separate droplets. After several such fissions, the electrostatic repulsion between ions on the surface of the remaining small charged droplets results in high electric fields near the liquid-vacuum interface, providing conditions suitable for field evaporation of ions from the liquid. Thus field assisted evaporation of cluster ions from the stable multi-charged droplets is the last stage in the generation of the gas phase ions in the ESI method. For water solutions, ion evaporation conditions are established at a droplet diameter of several tens of nanometers [2].

Another approach to the generation of ions by their extraction from liquids was proposed by Yakovlev et al. [3]. To avoid spraying the liquid, a polymer track membrane with nano-size channels was used for stabilization of the liquid in the strong electric fields. This stabilization required the electric forces acting on the liquid interface to be counterbalanced by surface tension [4]. The method can provide field evaporation of cluster ions and their direct introduction from glycerol/water solutions into the vacuum chamber of a mass spectrometer (MS) without loss of ions. The main principles of ion generation in this membrane ion source have been reported [4]. As with ESI, this method is described as "soft ionization" as no ion fragmentation occurs.

The possibility of applying such membranes for generating ions at atmospheric pressure was demonstrated in [5] for water and water/alcohol mixtures. Although the new atmospheric pressure technique was promising as it achieved high efficiency of transfer of liquid phase ions into the gas phase, long-term instability in the ion yield from the liquid was observed, despite the relatively high stability of the current maintained through the membrane.

It seems that the main difference between membrane ion extraction at atmospheric pressure compared with direct extraction into a vacuum is the limitation in the electric field strength imposed by the electric breakdown within the gas. In this case,

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pulsing of the electrical discharge between the membrane and the extracting electrode leads to corresponding pulses in the yield of ions from the liquid within the channels of the membrane.

As yet the specific mechanism of ion extraction from the liquid in the atmospheric pressure membrane ion source is not clear and its elucidation requires further investigation. Nevertheless, the application of multi-channel membranes may initiate a new direction in the generation of the gas phase ions of bioorganic substances. Importantly, the membrane interface may provide an alternative to the widely used ESI method in biological HPLC/MS. From this perspective, it is necessary to understand some properties of the interface related to its ability to carry out the analysis under a variety of conditions. In particular, it is highly desirable that the ions extracted from a multi-component solution of several compounds accurately reflect the ion composition of the sample. For identification of the various components by HPLC/MS, it is necessary to provide stable operation of the interface during the period of chromatographic separation. Ideally it should also be compatible with the various solvents typically used for optimal HPLC.

The aim of the present study was to monitor the properties of a membrane interface with the particular objective of evaluating its use in tandem methods such as HPLC/MS. Reducing the energy of the breakdown pulses was considered as a way of overcoming the long-term instability in the ion yield from the liquid. A possible design of the ion source with low energy discharge pulses is suggested. In addition, an experimental investigation of the ion current was carried out as a first step towards determining the mechanism of ion production in the atmospheric membrane ion source. It is anticipated that this will contribute to achieving long term stability in the operation of the membrane ion source.

2. Experimental

The experimental set-up used for identification of ions extracted from the membrane at atmospheric pressure is shown in Fig. 1. This is very similar to the design used in [5] but there is an additional possibility to provide a flow of the liquid sample so that a small amount of sample comprising a few μL fills the shallow cavity behind the membrane. The flow of the liquid sample was 200 μL/h.

To provide a more suitable integration with the membrane ion source, a short metal capillary of 5 mm in length and ID = 0.29 mm, OD = 0.72 mm was added to the atmospheric inlet of the MS. This capillary also served as the extracting electrode. The distance between the membrane and the inlet capillary was about 0.3 mm. A voltage of up to 3 kV was applied between the metal mounting of the ion source and the inlet capillary through a 1 GΩ resistor. A series of breakdown pulses stimulated the yield of ions from the membrane channels containing the sample solution. A typical value of the total current in the discharge chain was about 10–100 nA.

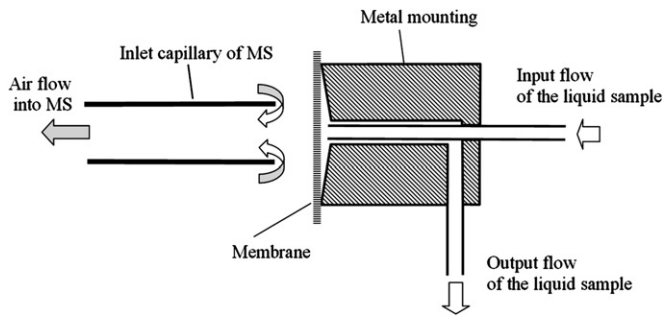

Fig. 1. The membrane ion source used for the mass spectral investigation of ions extracted from liquid solutions at atmospheric pressure.

Extracted ions together with the air flow passed through the inlet capillary of a commercial o-TOF mass spectrometer (Applied Biosystems Mariner) to be recorded as a mass selected ion current.

Another design of membrane interface was used to investigate the kinetics of the discharge current after the breakdown of the gas between the membrane and the metal extractor (see Fig. 2). To decrease the energy of the discharge, the electric capacity of the gas-filled electrode gap was minimized by using a sharp needle electrode-extractor located close to the membrane surface. In this case, the carrier air flow removing the ions from extraction zone was directed parallel to the membrane surface.

A voltage of up to 3 kV was applied to the liquid electrode through a 2.5 GΩ resistor. The ion current was recorded on an oscilloscope by monitoring the voltage developed across a 100 Ω resistor connected to the extracting electrode.

The poly(ethylene terephthalate) membrane was about 10 μm thick. The channel density was from 10^7 to 10^9 cm^{-2} and the diameter of the channels estimated from the air flow through the dry membrane was in the range 300–700 Å.

3. Results and discussion

3.1. Analysis of extracted ions

Peptide analysis: As reported previously, peptides ionized with the membrane source exhibit multiply protonated ions similar to those typically observed in ESI.

Fig. 3 shows a spectrum obtained by track membrane ionization of a mixture of gramicidin S and angiotensin II, each at a concentration of 5 μM in 40% acetonitrile acidified with 0.1% formic acid, i.e. solvent conditions that are typical of ESI. The cyclic peptide gramicidin S is widely used in ESI as a mass calibrant and is well known to show a weak singly charged molecular ion at m/z 1141.72 and a strong doubly charged ion at m/z 571.36 but no ions of higher charge states. By contrast angiotensin II with two basic residues and a free amino terminus gives singly, doubly and triply charged ions at 1046.54, 523.77 and 349.51, respectively, in ESI. All of these ions are observed in the spectrum shown in Fig. 3 and the isotope spacing confirms the charge state in each case.

Decreasing the average current of the ion source in comparison with that used in [5] gave enhanced long-term stability of the ion current. As seen in Fig. 4, the time available for uninterrupted work with the ion source can be more then 30 min, and when used with a fixed small volume of liquid, is similar to nanospray.

Analysis of proteins. The largest molecule previously reported to have been ionized with the membrane source was bovine ubiquitin

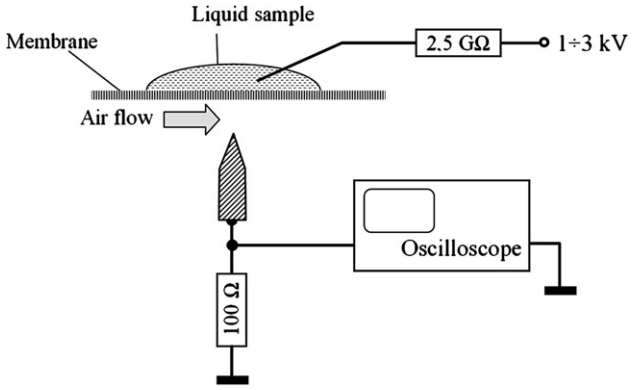

Fig. 2. Schematic diagram of the membrane interface used to investigate the discharge current kinetics in the system liquid/membrane/gas.