Ionization of Unpolar Molecules by Alkali Ion Attachment on the Surface of Electrolytic Solutions Exposed to High Electric Fields

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It is shown that mixtures of salts with low vapor pressure organic compounds deposited on field anodes can be used for surface ionization of paraffins by Li^+ and Na^+ ion attachment. The highest ionization efficiencies were obtained with emulsifying agents such as Tweens® mixed with LiI.

In previous papers [1 – 3] the ionization of molecules by alkali ion attachment on the surface of salt layers deposited onto field anodes (i. e. 10 μm W wires) has been reported. The attachment reaction results from a field induced and thermally activated charging of the salt layer with loosely bound alkali ions [4] which are captured by molecules striking the surface. Since molecules have the highest affinity values for Li^+ ions, lithium salts and in particular LiI were found to be most suitable for this mode of ionization.

It has been shown that the ionization efficiencies are orders of magnitude higher for polar than for unpolar molecules [3]. However, the small $(M+Li)^+$ ion currents obtained for example with paraffins are not only due to the low Li^+ affinity of M but also result from the high thermal activation (i. e. higher anode temperatures) needed to liberate Li^+ ions from the salt layer (since the anode temperature affects the adsorption of molecules, which is a prerequisite of the attachment reaction). In order to increase the ionization efficiencies for paraffins a Li^+ ion source operating at lower temperatures is necessary. In the search for such a source it was found that the most effective media for the ionization of paraffins by Li^+ ion attachment are not salts but electrolytic solutions i. e. mixtures of salts and organic compounds.

Electrolytic solutions from which a high Li^+ ion current could already be extracted at room temperature (RT) were prepared by mixing LiI and water with a number of compounds having a low vapor pressure in the liquid state such as polyvinyl alcohol, polyglycol, polyethers etc. The mixtures were deposited onto 10 μm W wires. The ion emission was obtained by applying field strengths of some 10^8 V/m i. e. a voltage difference of several kV between the wire and a counter electrode 3 mm away from it.

Optimum properties were found for Tweens® (polyoxyethylene fatty acid esters) which are emulsifying agents used for drug incorporation [5]. The maximum $(M+Li)^+$ ion current was not registered at RT but at elevated anode temperatures An example of a mass spectrum is shown in Figure 1. The $(M+Li)^+$ peak is stronger by a factor of about 50 than that obtained in previous experiments with LiI alone. In addition to the $(M+Li)^+$ signal ions formed by Na^+ ion attachment are also present in the mass spectrum; these result from a sodium content of the surface layer. In comparison with the $(M+\text{alkali})^+$ ions, the M^+ molecular ion of 2,2 dimethylpropane (neopentane) is extremely unstable, decomposing by the elimination of $CH_3^{\cdot}$. Field ionization signals could be avoided by heating the W wires to temperatures of about 2000 K before use, which leads to the formation of a smoother wire surface.

One treatment of the anode was found to be sufficient to maintain an intense $(M+Li)^+$ ion beam for more than one hour. The intensity fluctuations always decreased with increasing anode temperature. Under conditions of highest $(M+Li)^+$ emission the intensity fluctuations were about 20%. With electrolytic solutions the energy distributions of the Li^+ and $(M+Li)^+$ ions are broader than with pure salts due to a potential drop across the surface layer. This potential drop could be reduced by keeping the deposited layer on the anode surface thin. Additional peaks in the mass spectra corresponding to field desorption of the organic compounds (again via alkali ion attachment) could not be avoided. With Tweens® these peaks appeared in the mass range $> m/e$ 120 and increased with temperature. Since technical products were used it is hoped that a purification will reduce the number of such peaks particularly in the lower mass range.

The low anode temperatures and low field strengths at which a strong Li^+ ion emission and thus also the formation of $(M+Li)^+$ ions are observed can be described to the small amount of energy needed to dissociate the salt and solvate Li^+ ions in the organic matrix, to a low activation energy for ion migration, and in particular to a small work function for transfer of Li^+ ions from

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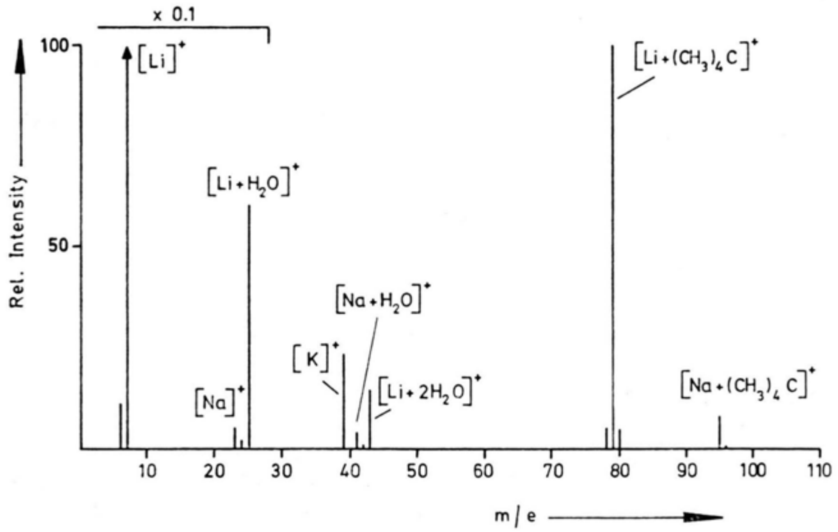

Fig. 1. Mass spectrum of 2,2-dimethylpropane (neopentane) obtained by alkali ion attachment on the surface of a mixture of Tween 20® (sorbitan monolaurate polyoxyethylene) and LiI (proportion in weight 1 : 1) exposed to a high external electric field. The mixture is deposited on a 10 μm W wire anode from aqueous solution. Anode heating current 15 mA.

the organic layer to the gas phase. The negative charges are neutralized by electron transfer processes at the phase boundary metal/layer accompanied by chemical reactions. This assumption is supported by the observation of a strong corrosion of the tungsten wire surface after the measurements. Furthermore it must be taken into consideration that the electrolytic solution prepared by mixing of LiI with the above mentioned compounds is not an homogeneous one. The emulsifying properties of Tweens® for example lead to the formation of small H_2O-salt droplets surrounded by organic molecules which act as a permeable membrane for the transfer of ions from the aqueous droplet to the gas phase in a high external field.

The new ion source is of particular interest for producing high $(M + \text{alkali})^+$ ion currents with unpolar or weakly polar molecules in order to study the decomposition behaviour of these ions following collisional activation [6, 7]. In addition the mechanism of ion formation represents an attractive new field of research.

Acknowledgement

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