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FIELD ION EMISSION FROM LIQUID SOLUTIONS: ION EVAPORATION AGAINST ELECTROHYDRODYNAMIC DISINTEGRATION

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Abstract - In several ionization techniques currently applied in organic mass spectrometry a mechanism of field induced ion evaporation from charged droplets is assumed to play a dominant role in the desolvation of ions from liquids. This ion evaporation mechanism is briefly discussed regarding its competition with electrohydrodynamic disintegration of the surface of the liquid droplet under field stress. It is shown that ion evaporation is unlikely to occur for most solute/solvent systems and of no significance in the formation of gaseous ions. In contrast electrohydrodynamic disintegration processes can contribute to the desolvation of ions from charged droplets.

In a number of ionization techniques currently applied in organic mass spectrometry molecular ions are formed in the gas phase by desolvation from liquids. Among these are the so-called electrospray /1,2/, ion-spray /3/, atmospheric pressure ion evaporation /4,5/ and thermospray ionization technique /6,7/ in which for ion formation out of the liquid phase the sample solution is sprayed into the gas phase. Since charged droplets are generated under these conditions, it is widely assumed that a mechanism of field induced ion evaporation as discussed by Iribarne and Thomson /4,8/ plays a dominant role in the formation of molecular and other ions by these ionization techniques. Typical molecular ions are (M+H)+, (M+Na)+, (M+NH4)+ and (M-H)- ions which are formed by proton, alkali and ammonium ion attachment and proton abstraction, respectively, already in solution under appropriate conditions. Such conditions are, for example, the availability of protons from acids, and alkali and ammonium ions from salts in the solution.

In any mechanism of ion evaporation, in which the ion leaves the surface of a charged droplet in a similar way as neutral molecules in a thermal evaporation process, an important prerequisite is the stability of the surface with respect to its electrohydrodynamic disintegration as result of the field stress on the surface. The maximum field strength (E_R) which can exist on the surface of a charged droplet under equilibrium conditions i.e. without disintegration of the droplet, is given by the well-known Rayleigh limit /9/

\[ E_R = \text{const} \cdot (\gamma / R)^{1/2} \]

with \( \gamma \) = surface tension and \( R \) = radius of the droplet. Since electrohydrodynamic disintegration processes may develop slowly, depending on the viscosity of the liquid, even higher field strengths can be achieved on a metastable surface for a short time.

Solvent evaporation from charged droplets causes a continuous decrease of droplet radius and increase of field strength. Therefore a further
condition for the contribution of the ion evaporation mechanism to the desolvation of ions is important: The rate of ion evaporation during solvent evaporation must be sufficiently high to take off surface charges by this mechanism prior to the removal of charges by electrohydrodynamic disintegration processes.

Iribarne and Thomson /4,8/ discussed the kinetics of ion evaporation for small ions with water as solvent by model calculations. They showed for alkali and halide ions that the free energy of desolvation has a minimum for a small solvation sphere between 6 and 12 water molecules (\(\Delta G^0\) is between 55 and 65 kcal/mol). The free activation energy for ion evaporation from charged droplets was calculated by treating the evaporation as a first order reaction in the frame of the absolute reaction rate theory. For a required rate constant of \(10^6 \text{s}^{-1}\) a value of 9 kcal/mol was obtained. This result was then used to determine the critical surface field strengths (\(E_\text{c}\)) for ion evaporation. For \(E_\text{c}\) values between 1.5 and 2 V/nm were obtained. It turned out that for droplet radii smaller than about 15 nm the field strength given by the Rayleigh limit is higher than the critical field strength for ion evaporation. This result seems to prove the possibility of an ion evaporation mechanism and to support a significant contribution of this mechanism to the ion formation in the techniques listed above.

However, inspection of the model of Iribarne and Thomson reveals two critical points:

1. In the calculation of the critical field strength for ion evaporation assumptions are made which are hardly acceptable: In the potential drop from the center of the charge of solvated ions to the surface of the liquid, the screening of the field by polarized solvent molecules is neglected. Furthermore, the dependence of the image potential on the relaxation time of charge rearrangement in the liquid is not considered. For ions evaporating from a liquid in the nsec or subnsec range image force effects are probably negligible. Applying more realistic potential energy values for the ion evaporation mechanism critical field strengths (\(E_\text{c}\)) by at least a factor of 2 higher are calculated. (A detailed discussion of the potential energy diagram is beyond the scope of this paper). These field strengths are not smaller than the field strengths given by the Rayleigh limit for very small droplet radii.

2. The first step of the ion evaporation mechanism i.e. the removal of an ion with part of its solvation sphere from a charged liquid surface under field stress represents the onset of an electrohydrodynamic disintegration process on a molecular scale. In the further development of such a process a series of charged small droplets or particles is ejected via the formation of a jet. The emission or evaporation of a single ion with subsequent surface relaxation is very improbable for these conditions.

Although a mechanism of ion evaporation, similar to that of neutral molecules, from the surface of the charged liquids is very unlikely for solvated ions, such a mechanism may still be possible for ions with surface active properties.

A pure thermal ion evaporation from uncharged surfaces of solvent free samples has been observed for some quaternary salts in the solid and liquid state under conditions of a high rate of evaporation of neutrals /10,11,12/. Thus field assisted ion evaporation from a solvent free melt of ionic compounds is a possible process not only for the quaternary compounds but probably also for other ionic compounds under conditions of a high rate of volatilization of the sample and stable surfaces under field stress. The conclusion can be drawn that the
volatilization of small charged liquid or solid particles, formed by solvent evaporation in the above spray techniques, into neutrals and ions in the gas phase can contribute to the "desolvation" of ions under appropriate conditions.

The extraction and desolvation of ions from viscous liquids by a field induced process is most obvious in field desorption (FD) /13,14/ and electrohydrodynamic ionization (EH) /15,16/ mass spectrometry. These ionization techniques have not been listed above because the ion desolvation in FD and EH mass spectrometry does not depend on droplet formation. Studies of ion extraction and desolvation from viscous layers in FD mass spectrometry revealed a cooperative desorption mechanism in which the energy for desolvation of ions is supplied by a response of the charged surface to the field stress thereby causing a destruction of the surface on a molecular scale /17,18/. Accordingly, the emission of desolvated ions occurs from a transient state of protrusions formed by electrohydrodynamic disintegration of the layer. In EH mass spectrometry a cooperative desolvation mechanism can also be postulated to be induced by electrohydrodynamic disintegration of charged liquid surfaces under field stress. For FD and EH an ion evaporation mechanism has been proposed, too /19,20/. However, there is no evidence for such a mechanism. Moreover, curved surfaces of liquids as those present in FD and EH mass spectrometry are much less stable with respect to field induced electrohydrodynamic disintegration processes than surfaces of spherical droplets. Accordingly, the effect of thermal evaporation of cations from a liquid state of the salt as mentioned before could not be observed under FD conditions. In contrast under these conditions the liquid salt layer was removed by a burst of ion emission.

An important question left is that for the relation between the field strength at which solvated ions are emitted from charged droplets by an electrohydrodynamic mechanism discussed above and the field strength given by the Rayleigh limit. The Rayleigh limit is derived on the assumption of a continuous charge distribution and macroscopic properties of the fluid, thus disregarding variations of the charge density and properties of the fluid on a molecular scale. Therefore the Rayleigh limit cannot be used to exclude the onset of a surface disintegration on a very small molecular scale at field strengths lower than \( E_R \). However, field strengths significantly higher than \( E_R \) are required for the generation of higher order electrohydrodynamic disintegration processes corresponding to the initial formation of surface protrusions with small radii of curvature while for field strengths close to \( E_R \) the disintegration starts with elliptic deformations /9/. Therefore it is not very probable that the onset of a disintegration of a droplet surface on a molecular scale is possible below \( E_R \).

The electrohydrodynamic disintegration of charged droplets at field strengths above the Rayleigh limit leads to the ejection of a series of small droplets. The size of these droplets very much depends on the kinetics of evolution of the disintegration process i.e. on the viscosity of the fluid and on the field strength at which the disintegration starts. Thus large deformations of a charged surface at the beginning of disintegration can develop to jets of very small droplets and even of partially desolvated ions. In our opinion this is the only field induced mechanism which can play a major role in the desolvation of ions from charged droplets i.e. in the above spray techniques. The contribution of the ion evaporation mechanism for desolvation of ions cannot be ruled out but is probably restricted to very special conditions as discussed above and is without practical significance.
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