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The solvent shells of cluster ions produced by direct electric field extraction from glycerol/water mixtures

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Electric field extraction of gaseous negative ions directly from water/glycerol solutions by use of a track membrane technique was investigated. The distributions of numbers of solvent molecules in the extracted cluster ions for different compounds were obtained. It is shown that the extraction mechanism is a direct field-stimulated evaporation of cluster ions from liquid, with a subsequent loss of several solvent molecules in the vacuum. For relatively simple ions a good correspondence of results was obtained with a continuous medium model. It was found that the number of solvent molecules in a cluster shell, for more complicated ions such as amino acids, is significantly greater than that for halide ions or ions of simple organic acids. An increase in the number of solvent molecules in the case of amino acid negative ions is rationalized in terms of the existence of several charged groups, each of which gives an additional contribution to the cluster shell. Copyright © 2001 John Wiley & Sons, Ltd.

The idea of using the direct extraction of ions from a liquid into the vapor phase in a strong electric field for the mass spectral analysis of solutions is, certainly, very attractive. The main difficulty is to provide a high electric-field strength sufficient to penetrate the polarization barrier and the stability of the liquid surface.

Two basic techniques have been developed to attain the appropriate conditions. The first involves spraying the solutions under investigation from the tip of a micron-size capillary in a strong electric field. Electrostatic dispersion ('spraying') of liquid in an electric field has achieved wide acceptance in mass spectral analysis, especially of solutions of high molecular mass organic substances and biochemicals.[1] Several consecutive processes, including generation of charged droplets, evaporation of solvent molecules, and break-up of the multicharged droplets, lead to cluster ion formation at atmospheric pressure. Additional pumping is required for introduction of the ions into a mass spectrometer. Mass spectral analysis based on electrospraying (ES) often requires additional processing of cluster ions or charged droplets in a collision chamber to release the ions from solvent molecules. Thus, ES is not direct introduction of ions from liquid solution into the vacuum analyzer of a mass spectrometer, for which additional technical difficulties emerge. However, the electrospray technique is now well established and is widely used. For example, the ES technique can be adapted to enable fragmentation of large molecules to provide structural information.[2]

The second technique is so-called electrohydrodynamic ionization (EHDI) (for a review see Ref. 3). As was found earlier,[4] under appropriate conditions ions can be released directly from the liquid. In the context of the electrostatic dispersion (spraying) of liquids, EHDI can be regarded as a limiting case of the conditions required to maximize the number of ions that can be extracted directly from a liquid.[5] In the EHDI techniques normally practiced, the liquid sample, usually a solution of the analyte in glycerol, is dispersed from the tip of a metal capillary biased at a voltage of 7–10 kV relative to an electrode placed in the vacuum. As was noted earlier,[6] the term 'electrohydrodynamic ionization' is misleading in the case of field extraction of ions from organic liquids like glycerol. The actual ionization is a purely electrolytic dissociation process in solution, and the electric field extracts only those solvated ions that exist at the surface of the liquid. The model of field evaporation through an intact liquid surface, proposed previously[6] for EHDI, has been criticized[5] because the release of an ion from a liquid can only occur via electrohydrodynamic instability of the liquid surface stressed by an electric field.[7] Optical investigations[8,9] have shown that the ion emission in an EHDI process occurs in the so-called 'rim mode', when ions are released from several discrete emission sites located along the rim of the capillary. It has been shown that this is a pulsed process with a frequency from 1 to 7000 Hz.[9] Both the instability of a liquid in an electric field and a requirement concerning the conductivity of the sample are the main problems of the method. Despite the fact that the use of the EHDI technique for MS has been less widespread than ES, a need for the creation of an ion source permitting direct introduction of ions from a liquid still remains.

New motivation for the realization of the idea of direct extraction of ions from a liquid comes from the demonstration of the possibility of creating an electromembrane ion source.[10,11] Use of a polymer track membrane with channels of submicron diameter allows the problems mentioned

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above to be overcome. The known combination of the liquid and the polymer base of the membrane provides a stable liquid surface, with curvature sufficient to counterbalance the combination of atmospheric pressure and the pressure due to electric field action.[12] So, it is likely that, under such conditions, we are dealing with a case of field evaporation of ions through an intact liquid surface. On the other hand, charging of the polymer base on the vacuum side of the membrane, supported by secondary processes, allows one to create a high local electric field which enables the effective transfer of ions from the liquid in the channels of such a membrane.[13] In contrast to EHDI, the electromembrane ion source does not require a sample of high electroconductivity and works even with pure glycerol. This 'soft' method does in fact provide ionization without fragmentation even for complicated organic ions. However, like EHDI, it does not allow gas-phase organic ions to be obtained without a solvent cluster shell. Indeed, the cluster ions consisting of a central ion and several solvent molecules were observed in previous investigations of this ion extraction method.[14,15] Thus, part of the solvent shell existing in a polar liquid is transferred into the gas phase together with the ion of interest.

We suggest that the structure of the cluster ions depends on the interactions between the central ion and solvent molecules, as well as on intermolecular interactions among the solvent molecules. The size of the cluster ion is determined by minimizing the energy needed for the transfer of this complex particle from the liquid into the gas phase. This energy is connected with polarization of the liquid by the ion and with breaking bonds between solvent molecules. One would expect an optimal size of the cluster ion released from the liquid, independent of the extracting electric field strength and the nature of the central ion. Indeed, the number of intermolecular bonds that must be broken to transfer a cluster ion from a liquid into the gas phase increases with increasing number of solvent molecules in the cluster ion, or the cluster ion size. On the other hand, an increase in the ion size decreases the polarization energy of the ion in the liquid. A more complex structure of the cluster ions may be expected for large nonsymmetrical molecules with several charged functional groups located at some distance from one another.

The objective of this work was an experimental determination of the composition of cluster ions extracted by an electric field from water/glycerol mixtures in the channels of the polymer track membrane and a determination of the influence of the structure of the dissolved substances on the nature of the mass spectra obtained by this method. The extraction of simple halide ions, as well as of negative molecular ions of organic acids including amino acids and several other more complicated substances, was investigated by mass spectrometry. We have also used this opportunity to evaluate the mechanism of field extraction of ions under conditions in which the liquid–vacuum interface is stable.

EXPERIMENTAL

A schematic diagram of the experimental set-up is shown in Fig. 1. The membrane ion source described previously[15] was used for the field extraction of ions from a liquid. A liquid sample in the form of drops was placed on the atmospheric-pressure side of a nonconductive poly(ethylene terephthalate) track membrane. The thickness of the membrane was about 10 μm, the channel density of the membrane was about 10^7 cm^{-2} and the diameter of the channels estimated from the air flow through the dry membrane was about 500 Å. The extracting electric field was created by two electrodes. One of them was sunk in the liquid sample and the other was a grid placed in the vacuum. At the minimum distance between the membrane and the extracting grid of about 0.4 mm, the extracting voltage was 1960 V.

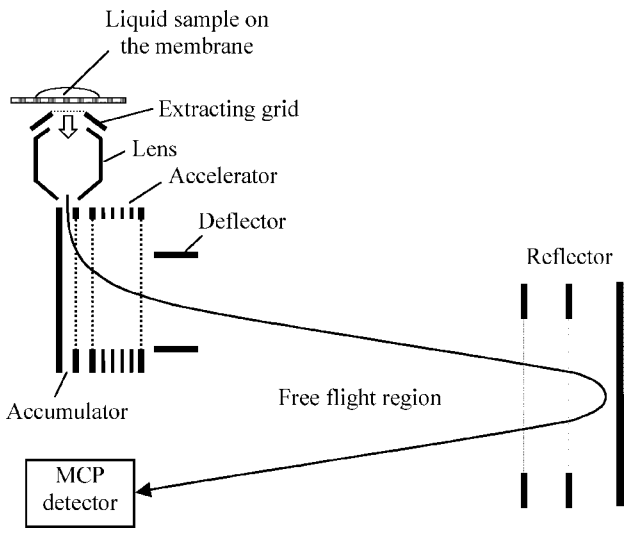


Figure 1. Experimental set-up for investigation of the field evaporation of ions from liquid solutions using the electromembrane ion source.

The identification of extracted ions was carried out with a time-of-flight (TOF) mass spectrometer with orthogonal acceleration.[15,16] The voltage between an electrode immersed in the liquid sample and the accumulator of the mass spectrometer was 300 V. All results were obtained for negative ions at room temperature.

The 'pure for analysis' grade of glycerol and 'special pure' grade salts of NaF, KCl, KBr, KI and $RbNO_3$, purchased from Reachim (Russia), were used to prepare the solutions without further purification. Distilled water was used in water/glycerol mixtures. Salicylic acid, acetylsalicylic acid, ascorbic acid, nicotinic acid, aspartic acid and glutamic acid were purchased from Sigma.

RESULTS

Mass spectra for all substances studied show series of peaks corresponding to the cluster ions $\{A^-Glycerol_n\}$ where A^- is the negative ion resulting from electrolytic dissociation of the dissolved substance, and n is the number of glycerol molecules in the cluster shell. Additionally, there were series of glycerol-only cluster ions $\{[Glycerol\text{-}H]^-Glycerol_n\}$ in the mass spectra.

The distribution of the peaks in the cluster series was practically independent of the extracting voltage. No significant differences in this distribution were observed

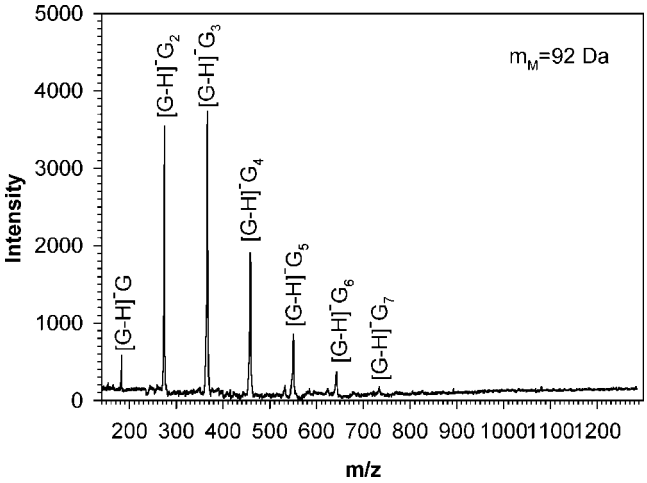


Figure 2. Mass spectrum for ion extraction from pure glycerol.

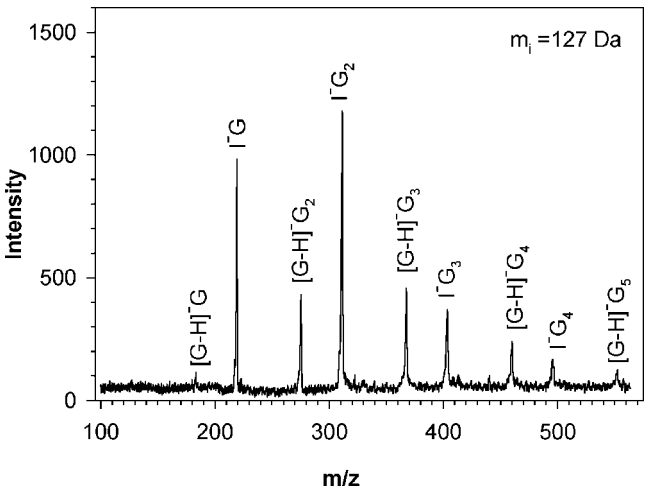


Figure 3. Mass spectrum for a 1×10^{-2} M solution of KI in glycerol.

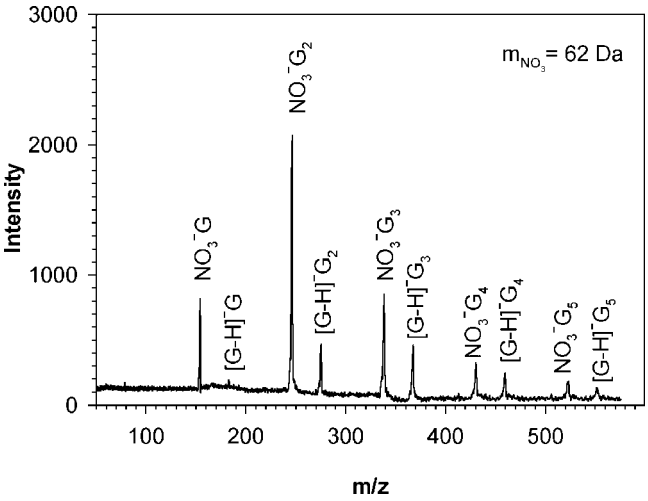


Figure 4. Mass spectrum for a 2×10^{-2} M solution of $RbNO_3$ in glycerol.

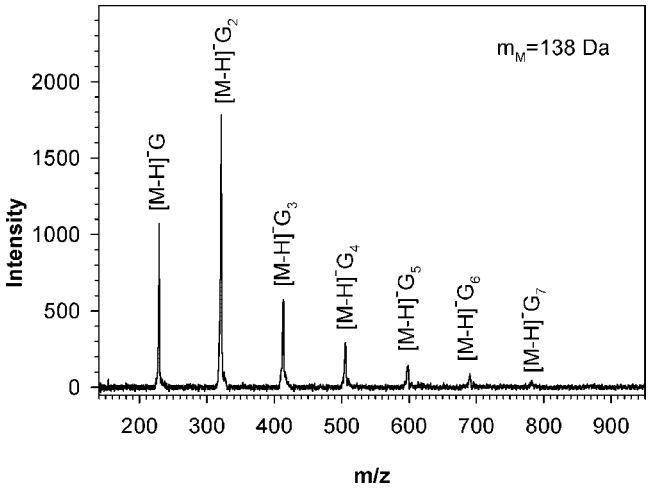


Figure 5. Mass spectrum for a 2×10^{-2} M solution of salicylic acid in a glycerol/water/ethanol mixture (volume ratio 4:1:1).

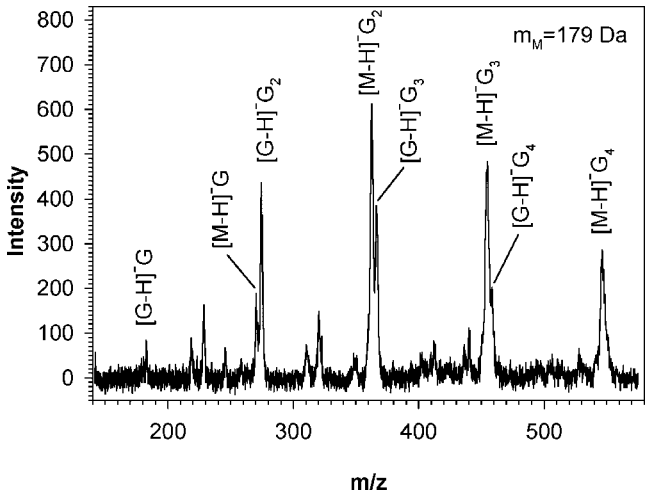


Figure 6. Mass spectrum for a 6×10^{-2} M solution of acetylsalicylic acid in glycerol/water mixture (volume ratio 1:1).

by changing the glycerol/water volume ratio. This fact was specially verified for the pure glycerol/water mixture and for solutions of salts, for which solubility in the concentration range used did not depend on the glycerol/water volume ratio. Variations of the glycerol/water volume ratio for solutions of the organic acids were limited by the analyte solubility and the sensitivity of the device used. In this case, the variation of the glycerol/water volume ratio in the limited range resulted in a change in intensity of all peaks in the cluster series but with the same distribution. No water cluster ions were observed for any of the solutions used.

Figures 2–10 present mass spectra obtained by extraction of ions from glycerol/water solutions of several compounds. To avoid any effects connected with possible differences in the membranes, as well as nonreproducibility of the distance between the membrane and the extracting grid, we used the same membrane for the main part of the experiments, changing only the liquid sample.

All substances investigated can be separated into two groups. Solutions of the substances in the first group gave

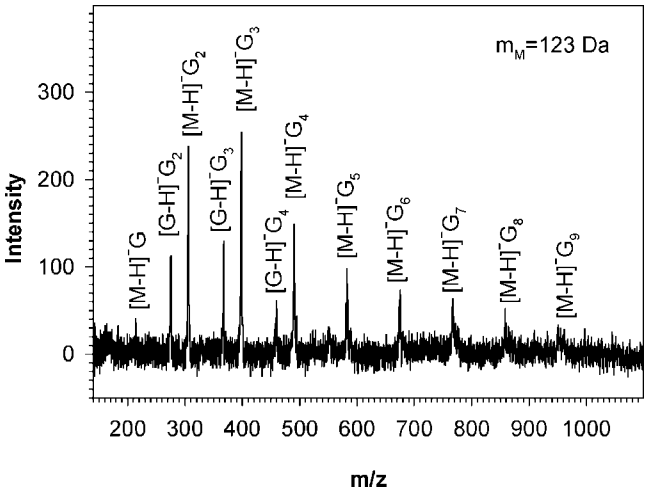


Figure 7. Mass spectrum for a 5×10^{-2} M solution of nicotinic acid in 3:2 glycerol/water mixture.

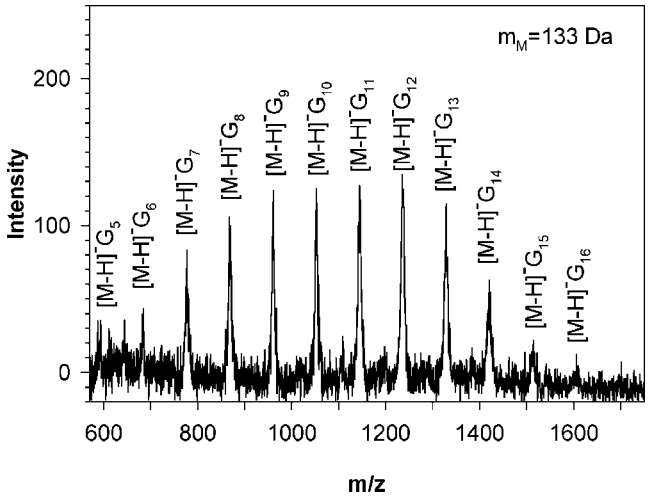


Figure 9. Mass spectrum for a 6×10^{-2} M solution of aspartic acid in 3:7 glycerol/water mixture.

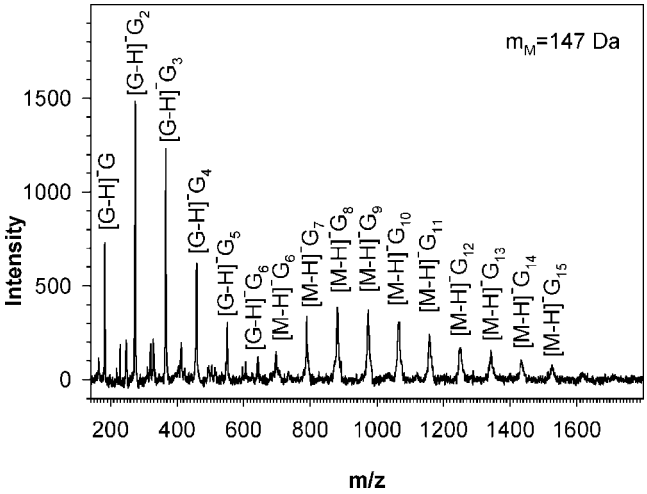


Figure 8. Mass spectrum for a 4×10^{-2} M solution of glutamic acid in 1:3 glycerol/water mixture.

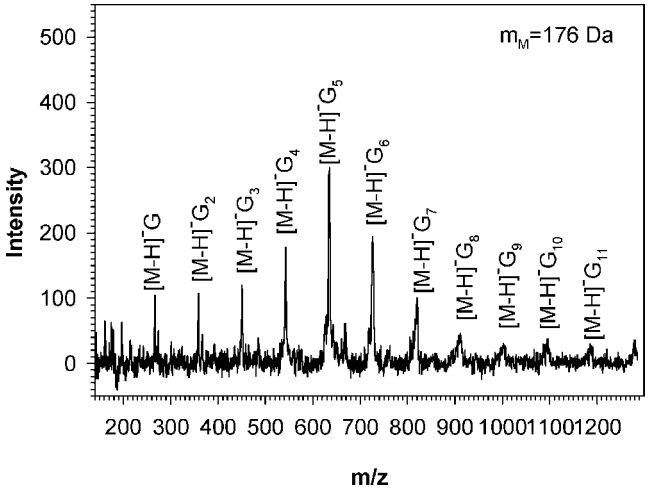


Figure 10. Mass spectrum for 1.1×10^{-1} M solution of ascorbic acid in water placed on the membrane with a trace of glycerol (volume ratio less than 1:10).

the mass spectra shown in Figs 2–7. The average number of solvent molecules in the cluster ions for such solutions was about 3. Deprotonated glycerol, halide anions, the NO_3^- anion and singly charged simple organic acid anions are in this group. The mass spectra given by this group are very similar to those observed earlier for glycerol cluster ions,[14,15,17] halogen ions[15] and nicotinic acid anions.[14]

Particular attention was paid to some substances of biological importance, such as amino acids. The mass spectra of ions extracted from glycerol/water solutions of two amino acids are presented in Figs 8 and 9. They represent a second group of substances. For these substances a maximum in the distributions of cluster peaks was observed at approximately 1000 Da. This value is greater than the molecular masses of the corresponding substances by a factor of about 8–10. The widths of the distributions of the cluster peaks were significantly greater than those of simple ions (first group), and the extraction efficiency was significantly lower.

The cluster shell observed in the mass spectrum of ascorbic acid (Fig. 10) had an average of 5–6 glycerol molecules, more than for the simple negative ions but less than for the amino acids. Thus, the solvent shells of the cluster ions and their extraction efficiencies were dependent on the size and structure of the central ion, but no significant influence of the glycerol/water ratio was observed.

DISCUSSION

It was found that only the $\{A^-Glycerol_n\}$ cluster series were present in the mass spectra of solutions in pure glycerol and for water/glycerol mixtures. It might have been expected that, for extraction from water/glycerol mixtures, $\{A^-(H_2O)_n\}$ cluster ions with the more polar water molecules would be observed. The absence of such cluster ions, even for solutions with a water/glycerol volume ratio greater than 1:1, probably indicates that the concentration of the water molecules near the liquid-vacuum interface is significantly lower than the concentration in the bulk due to evaporation of the water molecules.

Two questions are very important for understanding the

mechanism of ion beam formation in the electromembrane ion source. The first is connected with the mechanism for generation of primary cluster ions. As noted previously,[12,13,15] field evaporation of ions is the most likely mechanism for the field-assisted extraction when the liquid-vacuum interface is stable. The second question relates to subsequent changes in the primary ions extracted from a liquid. This question may be formulated briefly, as follows: how do the mass spectra reflect the initial distributions of primary cluster ions with respect to the numbers of solvent molecules?

As observed, the numbers of solvent molecules in cluster ions (n), as recorded in the mass spectra, is not very large. This implies that a robust theory for the process should take into consideration microscopic descriptions related to cluster ion composition and interactions between its different parts. On the other hand, we are not yet ready to establish a definite connection between the experimental distributions observed in the mass spectra and the primary ion composition. As noted previously,[15] the internal energy of the cluster ion after transfer from the liquid to the vacuum may be enough to break one or more bonds between solvent molecules and the central ion (and possibly other molecules forming the cluster ion). So, a unimolecular decay of the cluster ions:

$$\{\mathrm{A^-Glycerol}_n\} \rightarrow \{\mathrm{A^-Glycerol}_{n-1}\} \rightarrow \cdots \rightarrow \{\mathrm{A^-Glycerol}_k\} \quad (1)$$

seems quite feasible as a mechanism for formation of the recorded ion beam, if we take into account the kinetic energy distributions of ions in beams produced by the membrane ion source, reported earlier.[15,18] An observed shift in the kinetic energy distribution can be attributed to a loss of several solvent molecules immediately after extraction of the cluster ion. This process was also observed in EHDI-MS.[19]

Bearing in mind all the circumstances mentioned above, the extraction of ions from the liquid in the channels of the membrane can be considered from the viewpoint of a model involving field evaporation from a continuous liquid. Such an approach is quite feasible for charged droplets when the number of solvent molecules is sufficiently large. Use of such a model justifies use of the surface tension coefficient as a measure of a solvent-solvent interaction. For the sake of simplicity we shall consider the cluster ions as spherically symmetric species.

The activation energy for ion evaporation from a liquid is the sum of the evaporation energy of the appropriate neutral particle and the polarization energy of the ion in the liquid.[12] In our approximation, the activation energy for the field extraction may be expressed in the form:

$$\Delta E = E_s - U_p - \delta E(F) \quad (2)$$

where E_s is the surface energy of the cluster ion after extraction, U_p is the energy of the polarization interaction between the cluster ion and the liquid, and $\delta E(F)$ is a depression of the potential barrier due to an electric field of strength F applied to the liquid-vacuum interface. In the simplest case the field-dependent depression of the energy barrier can be described by the well-known Schottky form:

$$\delta E(F) = e(eF)^{1/2} \quad (3)$$

where e is the charge on the ion. This term does not depend on the size of the ion extracted and affects only the extraction efficiency.

The most probable radius of the cluster ion extracted can be obtained from the minimum of the activation energy, i.e. for the condition $\partial(\Delta E)/\partial r = 0$. In the context of the model under consideration, one can use the Born approximation for U_p:

$$U_p = -e^2(1 - 1/\varepsilon)/(2r) \quad (4)$$

where ε is the dielectric constant of the liquid and r is the radius of the cluster ion. E_s is given by:

$$E_s = 4\pi\sigma\ r^2 \quad (5)$$

where σ is the surface tension coefficient of the liquid. Thus, the condition for the optimal cluster ion radius (the radius when the evaporation probability is maximal) can now be expressed as follows:

$$\partial[e^2(1 - 1/\varepsilon)/(2r) + 4\pi\sigma\ r^2]/\partial r = 0 \quad (6)$$

This equation gives the following expression for the optimal radius of the cluster ion:

$$r_{opt} = [(e^2/8\pi\sigma)(1 - 1/\varepsilon)]^{1/3} \quad (7)$$

Relationship (7) gives $r_{opt} = 4.2$ Å, if one uses values of $\varepsilon = 42$[20] and $\sigma = 62$ dynes/cm[20,21] known for glycerol at a temperature near $T = 300$ K. In this case $U_p(r_{opt}) = -1.7$ eV and $E_s(r_{opt}) = 0.85$ eV. So, the theoretical energy barrier for extraction of such an 'optimal' ion is 2.55 eV. Similar calculations were made previously for water cluster ions evaporated from droplets.[22]

A connection between the number of solvent molecules in the cluster ion and the size of the cluster ion components can be obtained in the following way. The total volume of the cluster ion v is approximately equal to the sum of the volumes of its components:

$$v = v_i + nv_s \quad (8)$$

where v_i is the volume occupied by the central ion and v_s is the volume related to one solvent molecule. Taking the relation between the volumes and corresponding radii in the form $v = 4\pi r^3/3$, the number of solvent molecules in the cluster ion can be calculated from the relationship:

$$n = (r/r_s)^3 - (r_i/r_s)^3 \quad (9)$$

where r_i and r_s are radii of the central ion and a solvent molecule, respectively.

If we suppose that the distribution over r of the cluster ions initially evaporated can be represented as:

$$\mathrm{w}(r) = \mathrm{A}\ exp(-\Delta E/kT) \quad (10)$$

where A is a coefficient independent of r and k is the Boltzman constant, then the distribution of the primary ions over n can be obtained as follows, taking into consideration Eqn. (2),

$$I(n) = I_0\ exp\{-[4\pi\sigma r_n{}^2 + e^2(1 - 1/\varepsilon)/(2r_n)]/kT\} \quad (11)$$

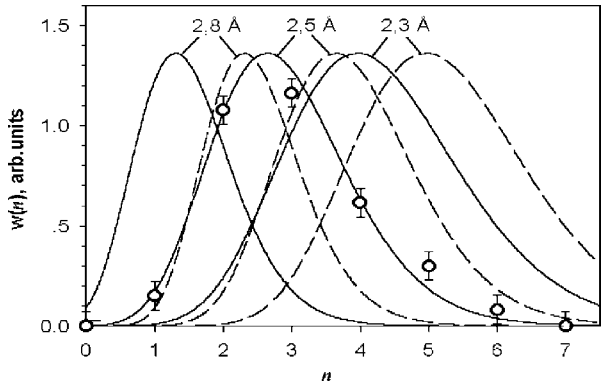


Figure 11. Comparison of the experimental data obtained from the mass spectra for the cluster ions {[Glycerol-H]$^-$Glycerol$_n$} extracted from pure glycerol with the distributions calculated by Eqn. (11) without decomposition of the cluster ions (dashed line) and with the loss of one solvent molecule after evaporation (solid line).

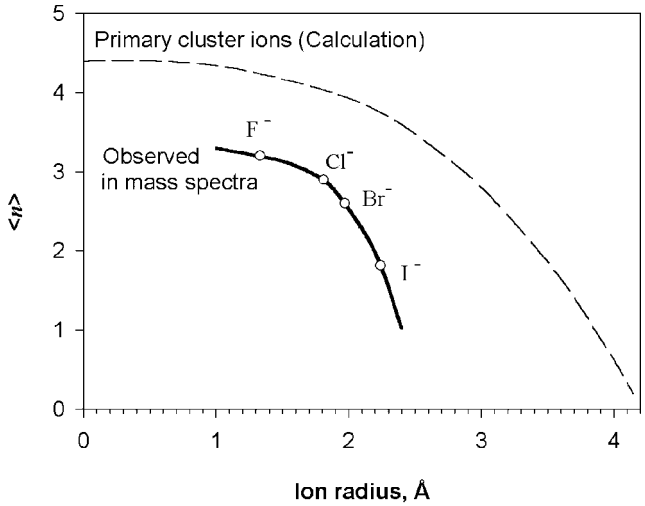


Figure 12. The dependence of the average number of glycerol molecules in cluster ions on the radius of the central ion, obtained for halide ions extracted from glycerol (solid line) and calculated from Eqns (9) and (11) (dashed line) at different radii of the glycerol molecule.

where r_n is the radius of the cluster ion having n solvent molecules, which is connected by Eqn. (9) with the radii of the cluster components, and I_0 is a constant independent of n. In this model, in accordance with our experimental results, the distribution is independent of F. (Note that no dependence of the distribution on the voltage applied to the capillary was observed in EHDI investigations also.[5])

To further test the model, a comparison of the calculated ion distribution with the experimental mass spectrum was carried out for the {[Glycerol-H]$^-$Glycerol$_n$} series. For the sake of simplicity we assumed that $r_i = r_s$. Formally, as the first step, the comparison of the model was carried out in the (assumed) absence of any cluster ion decomposition. In this case, the calculated distribution can be compared directly with the observed mass spectra using the solvent radius r_s as a fitting parameter. It was found that, at all values of this parameter, the model can *not* provide an agreement between the calculated distribution and the experimental data within the experimental error (see Fig. 11).

The next step was to take into consideration the possible decomposition of the cluster ions after evaporation. In this case, due to unimolecular decomposition (Eqn. (1), each evaporated cluster ion (with a fixed initial number n of glycerol molecules) generates a new distribution $f_n(n_{new})$ over the number of the solvent molecules n_{new} in the (second generation) cluster ions. To obtain the best theoretical distributions for comparison with the mass spectra for each n_{new}, we should sum over all n the distributions, $f_n(n_{new})$, with weighting factors obtained from the field evaporation model. We are not in a position at present to perform such calculations, and we used instead an approximation that each evaporated ion lost the same number of solvent molecules (Δn). This assumption allows use of the number of solvent molecules lost after evaporation as a fitting parameter, together with the glycerol radius. Using this simplification, the calculated distribution can be compared with mass spectra after replacing n with $(n - \Delta n)$ in Eqn. (11). The best correspondence between the experimentally observed mass spectra and the results of calculations by Eqn. (11) was obtained at a glycerol radius of 2.5 Å and $\Delta n = 1$ (see Fig. 11). The FWHM of the distribution obtained at those parameters is about 2. The best-fit glycerol radius is close to that of 2.78 Å calculated from the density of liquid glycerol, with consideration for molecular packing, as:

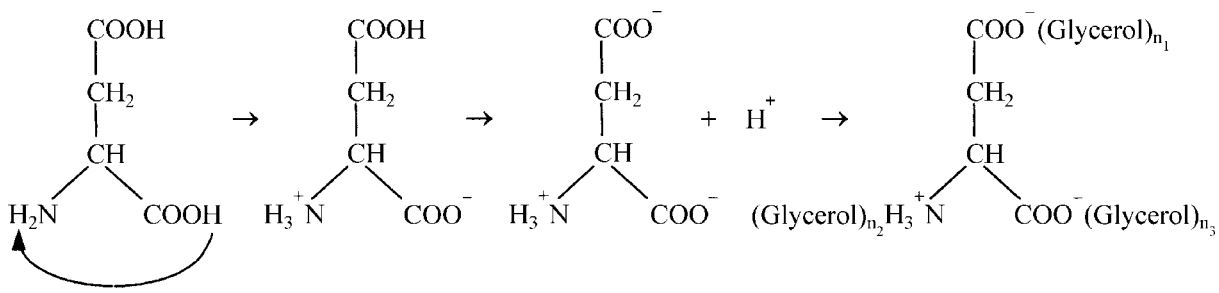
$$r = [(3/4\pi)(M/\rho N_A)\gamma]^{1/3} \quad (12)$$

where M is the molecular mass, $\rho = 1.26$ g/cm^3 is the density of liquid glycerol,[20] N_A is Avogadro's constant and γ is a packing coefficient assumed to be equal to the maximal value of 0.74 as for a hard sphere.

Using the value of the glycerol radius thus obtained, the average number of solvent molecules in the cluster ion evaporated $<n>$was calculated for the halide ions by the distribution expression (11). The result is presented in Fig. 12 together with the experimental data obtained from treatment of the mass spectra. The model under investigation correctly reflects the qualitative dependence of the average number of solvent molecules in the cluster ion on the central ion radius, but it gives a greater range of values of $<n>$ than that obtained experimentally. This discrepancy can be connected, as in the case of the {[Glycerol-H]$^-$Glycerol$_n$} cluster ions, with the loss of one or two glycerol molecules during the several microseconds before the mass spectral ions are detected.

It is surprising that use of a macroscopic (continuous liquid) model, for cluster ions with a small number of solvent molecules, yields a result very close to the experimental one. It is likely that this is due to the weak dependence of r_{opt} on σ (as the cube root, Eqn. (7)). So, such considerations are useful for an estimation of $<n>$. A more correct and exact description of the phenomenon will require more detailed consideration of interactions for all particles involved in the cluster ion formation.

In the case of the negative ions of simple organic acids, for which the charges are located in one part of the ion (see Figs 5–7), the average number of solvent molecules is close to that



Scheme 1.

observed for the {[Glycerol-H]$^-$Glycerol$_n$} series (Fig. 2). Thus, the polar solvent shell is retained after evaporation of such ions from glycerol with an average number of solvent molecules of 3–4.

A dramatic deviation from this simple model is observed in the case of amino acid solutions. A special feature of the evaporation of amino acid ions can be explained if the complicated charge structure of these substances is taken into consideration. It is likely that, in the case of large organic ions, the cluster shell is only formed near charge centers. Every charge-carrying region of an ion could have its own shell with about 3–4 solvent molecules, as for simple ions. Proton transfer from COOH to NH_2 gives two charged groups, NH_3^+ and COO^-, to form a zwitterion. Dissociative (electrolytic) ionization of the amino acid molecule in a polar solvent like glycerol results in three separate charge sites. For example, the formation of the shell of aspartic acid ion may be represented schematically by Scheme 1.

It would be expected that for such substances the cluster shell would have $n \approx 9$–12, and that the field evaporation of such ions would be more difficult compared with ions having a simple charge structure, such as halide ions or the anions of simple acids. This estimate ($n \approx 9$–12) is very close to the number of solvent molecules observed in the mass spectra.

The case of ascorbic acid is intermediate between the substances with a simple ionic charge structure and those with strongly localized charges on different functional groups. It seems likely that the polar (sugar-like) group of the ascorbate anion also contributes to cluster shell formation.

CONCLUSIONS

The direct evaporation of ions from polar liquids such as glycerol involves the transfer of ions from liquid into vacuum together with a portion of their solvation shells. For fairly small central ions, the shells of such cluster ions have an average of about 3–4 solvent molecules. When the central ion has a more complicated charge distribution, the solvent shell may have significantly more molecules, e.g. about 10 for amino acid anions. Thus, the solvent shell of ions produced by direct evaporation from liquid solution displays both a charge and a solvent structure determined by the nature of the ions in the liquid. Multiple charge sites on the central ions, as in the amino acid ions, lead to an increase in the number of solvent molecules in the cluster ion shell and to a decrease in extraction efficiency.

Acknowledgements

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