Observation of Triply Charged Metal Ion Clusters by Electrospray and Laser Spray

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Studies of the gas phase ion chemistry of triply charged metal ions, $M^{3+} = Sc^{3+}$, Y^{3+}, La^{3+}, Ce^{3+}, and Yb^{3+}, were made by electrospray and laser spray. Triply charged ion ligand complexes, $M^{3+}(ligand)_n$ were produced in the gas phase by electrospray and laser spray for the following ligands; glucose; sucrose; raffinose; cyclodextrin; ginsenoside Rb_1; dimethyl sulfoxide (DMSO) and hexamethylphosphoramide (HMPA). The ion evaporation mechanism must be invoked to explain the transfer of more surface active ions (e.g., $NH_4^+(H_2O)_n$) in solution to the gas phase, while the transfer of low surface active ions (e.g., $La^{3+}(sucrose)_n$) may be explained by the charged residue model. In general, the laser spray gives stronger ion signals than electrospray for aqueous and water/methanol solutions. The laser spray is found to be more suitable for the observation of ions with larger solvation energies (e.g., $Sc^{3+}(DMSO)_n$). These results may be due to the enrichment of the sample concentration by the selective vaporization of the volatile solvent on the tip of the stainless steel capillary and also to the finer droplet formation caused by the laser irradiation. Copyright © 1999 John Wiley & Sons, Ltd.

Metal ions play an important role in the function of many metalloenzymes. For example, the interaction of regulatory proteins such as calmodulin with other proteins depends on whether Ca^{2+} is specifically bound.[1,2] Studies of metal ion solvation provide information, not only about the metal ion chemistry in solution, but can lead to an improved understanding of the structure and functions of many biomolecules in which metal ion interactions play a role.

Multiply charged metal ions have not received much attention in electrospray experiments due in part to the belief that charge exchange occurs exclusively. Since doubly and triply charged ions exist in solution, preparation of gas phase ions such as $M^{2+}(solvent)_n$ and $M^{3+}(solvent)_n$ might be possible by transfer of multiply charged ions solvated in solution from the liquid to the gas phase. Although the ion signals were very low, Pelzer *et al.* observed some $M^{2+}(ligand)_n$ with fast-atom bombardment (FAB) and then only when large multidentate complexing agents were used, presumably because these stabilize the charge by extensive charge delocalization.[3] Later, Röllgen *et al.*[4] reported the observation of $Ca^{2+}(H_2O)_n$ and $Sr^{2+}(H_2O)_n$ using thermospray. These doubly charged ions should be easy to detect because the ionization energies (IE) of Ca^+(11.9 eV) and Sr^+(11.0 eV) are lower than that of H_2O(12.6 eV). Recently, Kebarle and co-workers found that $M^{2+}(H_2O)_n$ were formed as major gas phase ions when suitable liquid solutions containing the M^{2+} ions (M = Mg, Ca, Sr, Ba, Mn, and Co) were electrosprayed.[5] A variety of M^{2+} ion ligand complexes with the above and Cr^{2+}, Cu^{2+}, Co^{3+} with ligands such as dimethyl sulfoxide (DMSO), dimethylformamide, pyridine, and the polydentates: peptides, di- and polyketones, cyclic tetramines, and polycyclic hexamines, could also be observed. Beyer *et al.* made a similar observation for an aqueous solution of triply charged metal ion (M^{3+}) salts in electrospray, where only

$MOH^{2+}(H_2O)_n$ and no $M^{3+}(H_2O)_n$ were observed.[6] Quite recently, Kebarle extended the study of the gas phase ion chemistry to the observation of triply charged ion ligand complexes, $M^{3+}(ligand)_n$, produced in the gas phase by electrospray of a solution of the M^{3+} salts (M = Y, La, Ce, Nd, and Sm) and with the ligand DMSO.[7]

In the present work, the cluster ions of triply charged metal ions $M^{3+}(ligand)_n$ with M = Sc, Y, La, Ce, and Yb and with the ligand DMSO and hexamethylphosphoramide (HMPA) have been studied systematically in order to obtain information on the solvation of these ions in solution and in the gas phase by using electrospray and laser spray. Because metal ions play important roles as mediators for the function of the glycoprotein enzymes, sugar samples such as glucose, sucrose, raffinose, α-cyclodextrin and ginsenoside Rb_1 were also examined as ligands. A comparative study of electrospray and laser spray was also made.

EXPERIMENTAL

The instrumentation currently used is largely similar to that described previously for electrospray[8] and laser spray.[9,10] A stainless steel capillary (i.d. 0.13 mm, o.d. 0.3mm) parallel to the interface plate was supplied with sample solution by means of a computer-regulated pump (Tosoh CCPD, Akasaka, Tokyo, Japan). Nebulizer gas, N_2, effusing from the concentric stainless steel tube (i.d. 0.7 mm) reduced the angular divergence of the plume and entrained the mist and gas toward the sampling orifice.

For electrospray, a sample flow rate of about 5 μL/min gave the most intense ion signals with a voltage of about 3 kV applied to the capillary. For the laser spray, a SYNRAD (Bothel, WA, USA) model 48-5, Duo-Lase 50 W infrared laser (10.6 μm) was used. The tip of the stainless steel capillary was irradiated from the opposite side of the capillary by a laser beam focused to ≈0.1 mm. With a sample flow rate of about 100 μL/min, a laser power of ≈5 W and ~3 kV applied to the stainless steel capillary

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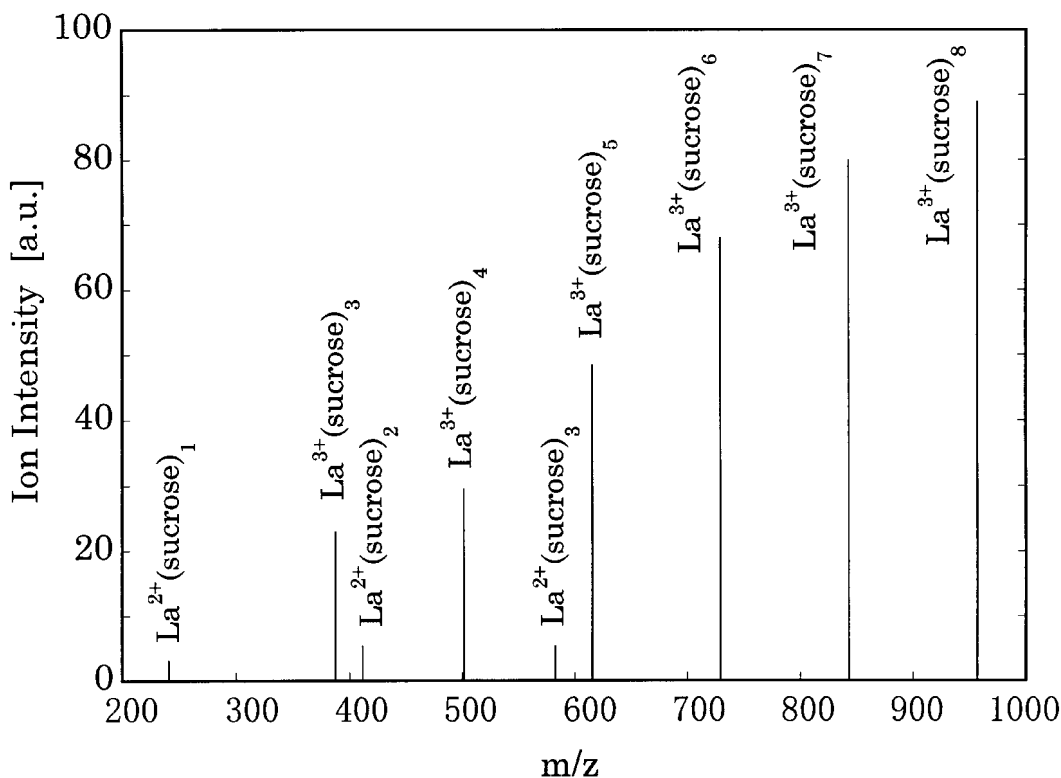
Figure 1. Electrospray mass spectrum for a H_2O/CH_3OH (1:1, v/v) solution of 10^{-5} M $LaCl_3$ and 5×10^{-4} M sucrose. The other major ions $LaOH^{2+}(H_2O)_n$ are omitted from the spectrum for clarity. The peak intensities are corrected taking into consideration the transmission efficiencies of the quadrupole mass spectrometer.

gave the most intense ion signals under the present experimental conditions. As described previously,[9] laser spray is applicable to a wide variety of samples such as amino acids, peptides, sugars, surface active agents, metal ions, halide ions, etc., for both positive and negative ion modes without any sample degradation. When the laser spot is properly focused on the center of the capillary tip, stable ion signals were obtained over the period of measurements.
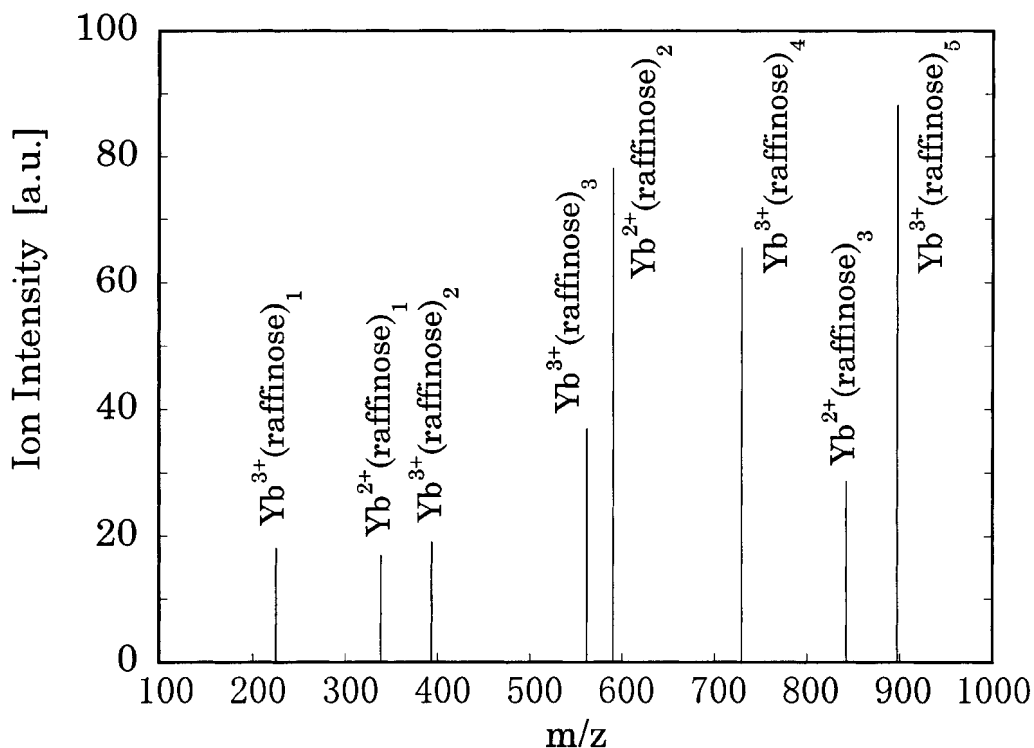
Figure 2. Electrospray mass spectrum for a H_2O/CH_3OH (1:1, v/v) solution of 10^{-5} M $YbCl_3$ and 5×10^{-4} M raffinose. The other major ions $YbOH^{2+}(H_2O)_n$ are omitted from the spectrum for clarity. The peak intensities are corrected taking into consideration the transmission efficiencies of the quadrupole mass spectrometer.
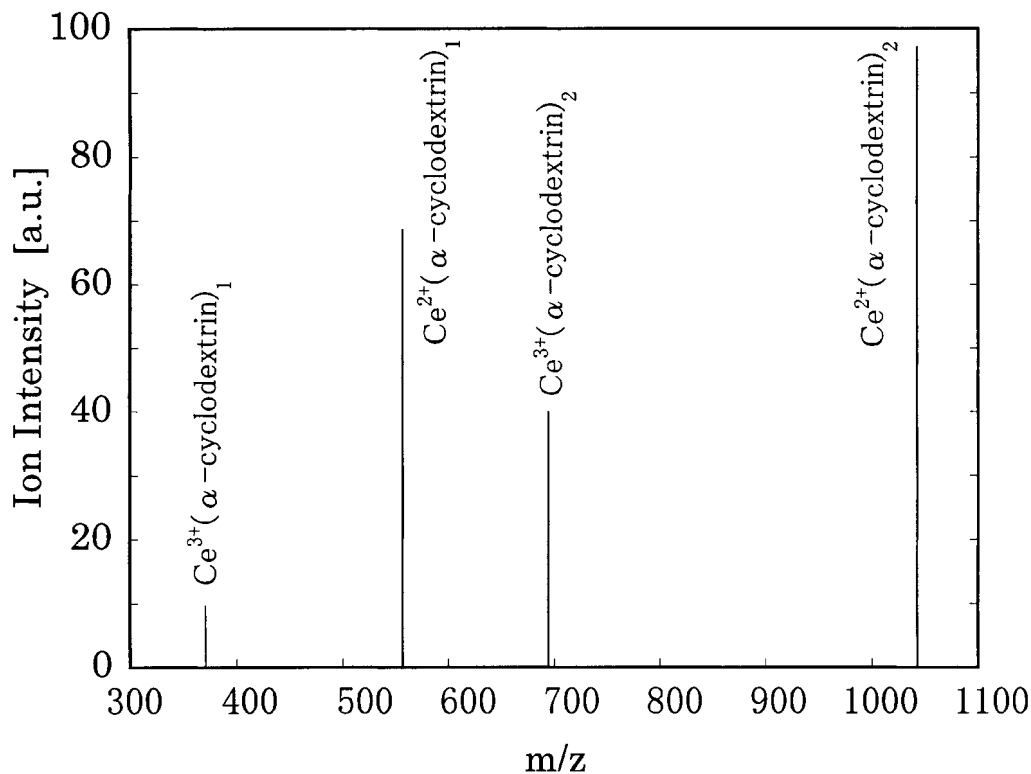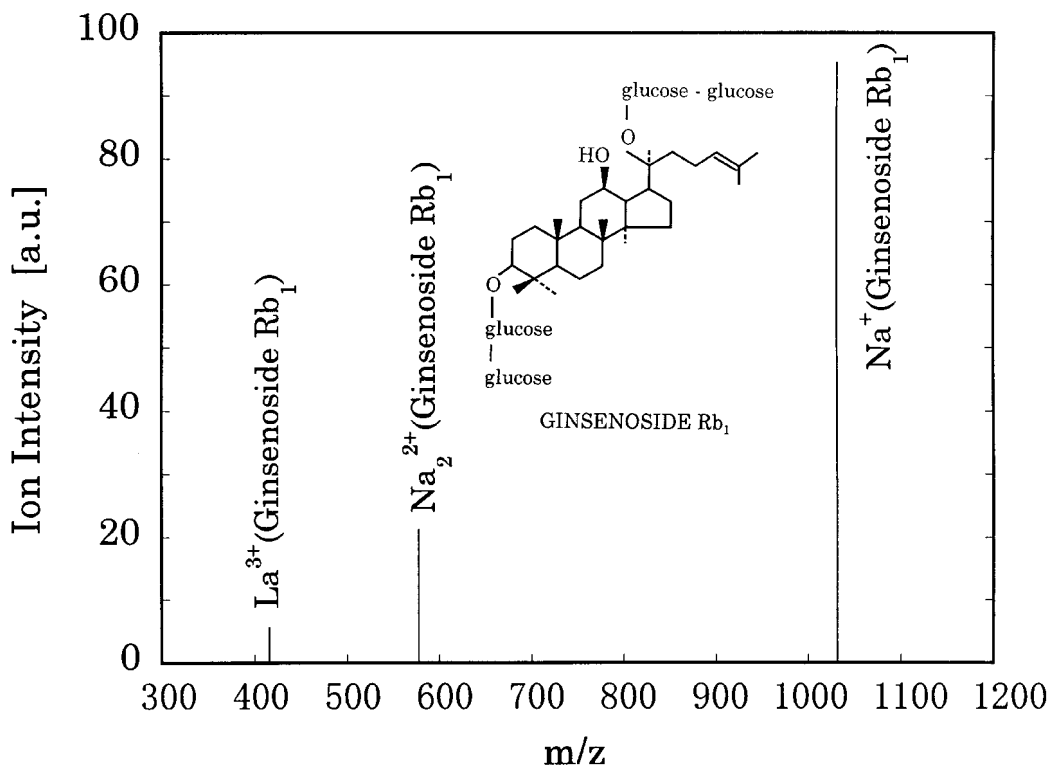
Figure 3. Electrospray mass spectrum for a H_2O/CH_3OH (1:1, v/v) solution of 10^{-5} M $CeCl_3$ and 5×10^{-4} M α-cyclodextrin. The other major ions $CeOH^{2+}(H_2O)_n$ are omitted from the spectrum for clarity. The peak intensities are corrected taking into consideration the transmission efficiencies of the quadrupole mass spectrometer.

For samples of aqueous solutions laser spray gives 5–10 times stronger ion signals than electrospray. For samples of H_2O/CH_3OH (1:1, v/v) solutions, the signal intensities obtained by laser spray are about the same or higher than by electrospray.

The ions formed at atmospheric pressure were sampled

Figure 4. Electrospray mass spectra for a H_2O/CH_3OH (1:1, v/v) solution of 10^{-4} M $LaCl_3$, 10^{-4} M NaCl, and 10^{-4} M ginsenoside Rb_1. The other major ions $LaOH^{2+}(H_2O)_n$ are omitted from the spectrum for clarity. The peak intensities are corrected taking into consideration the transmission efficiencies of the quadrupole mass spectrometer.
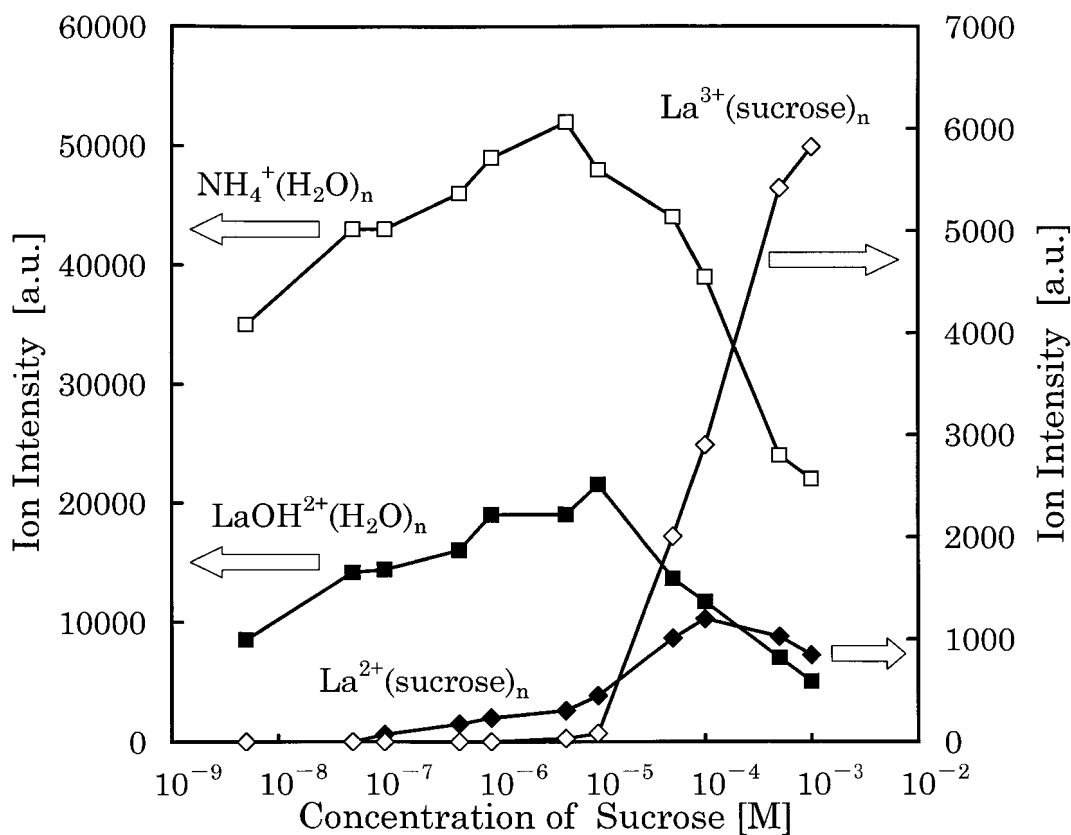
Figure 5. The intensities of $LaOH^{2+}(H_2O)_n$, $La^{3+}(sucrose)_n$, $La^{2+}(sucrose)_n$ and $NH_4^+(H_2O)_n$ as a function of sucrose concentration for a H_2O/CH_3OH (1:1, v/v) solution of 10^{-5} M $LaCl_3$ measured by electrospray. The intensity of ion(ligand)$_n$ corresponds to the value summed up for all n observed. The transmission efficiencies of the quadrupole mass spectrometer were taken into consideration.
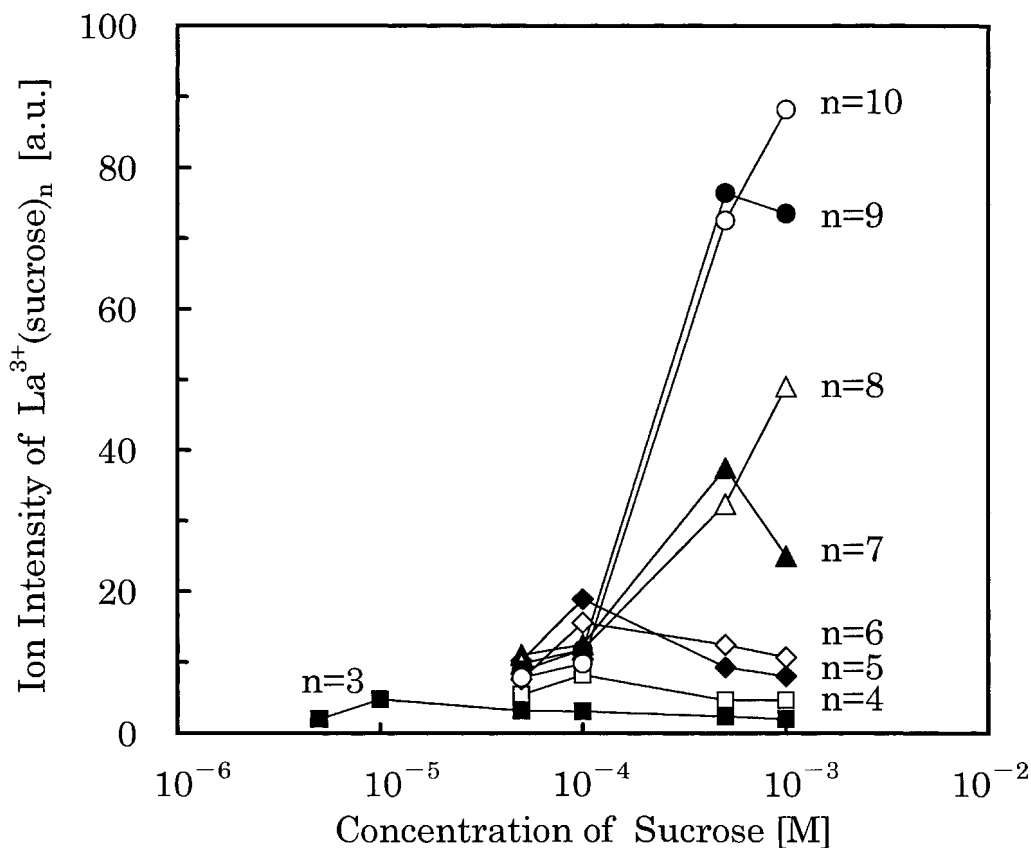
Figure 6. The intensities of $La^{3+}(sucrose)_n$ as a function of sucrose concentration for a H_2O/CH_3OH (1:1, v/v) solution of 10^{-5} M $LaCl_3$ measured by electrospray. The transmission efficiencies of the quadrupole mass spectrometer were taken into consideration.
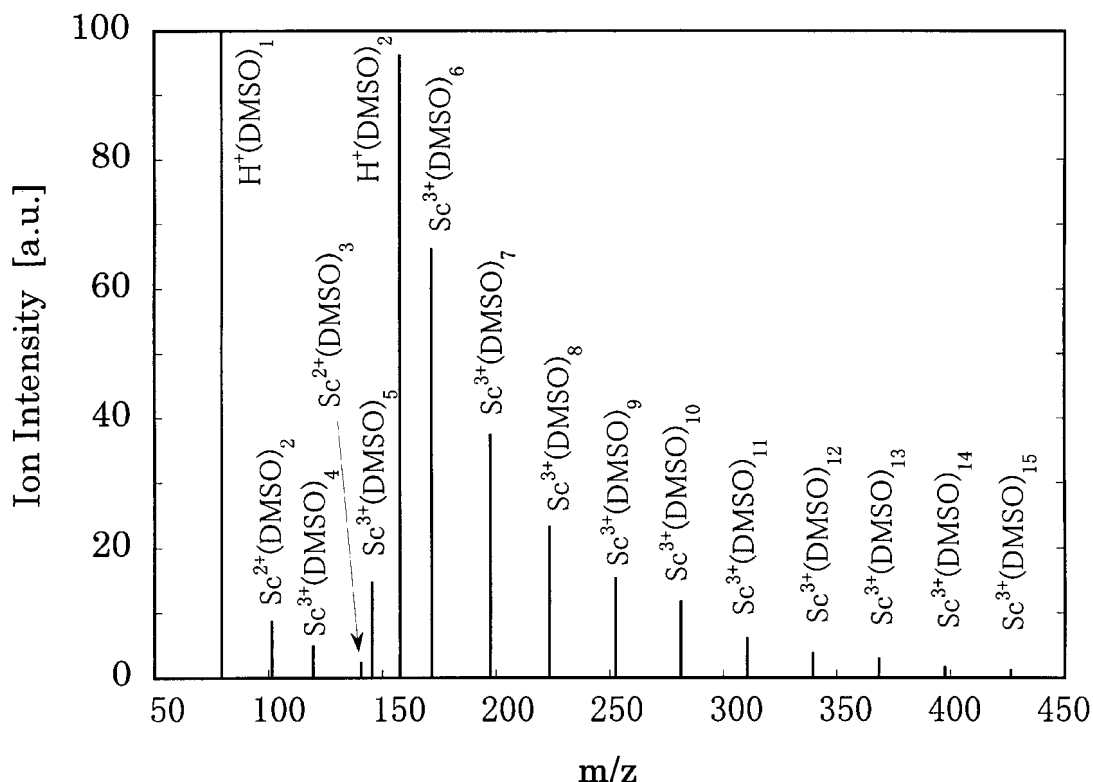
Figure 7. Laser spray mass spectrum for an aqueous solution of 10^{-5} M $ScCl_3$ and 2×10^{-1} M DMSO. The transmission efficiences of the quadrupole mass spectrometer were taken into consideration.

into the vacuum system through a 100 μm diameter orifice and mass analyzed by a quadrupole mass spectrometer, model MSQ-400 (ULVAC, Chigasaki, Japan) over the range m/z 5–1100.

The calibration of the transmission efficiency of the quadrupole mass spectrometer was made using tetraalkylammonium salts, $(C_nH_{2n+1})_4NBr$, with n = 1–10. In this experiment, a 5×10^{-6} M solution of several salts in H_2O/CH_3OH (1:1, v/v) was electrosprayed and the relative intensities of $(C_nH_{2n+1})_4N^+$ ions were measured. It was assumed that the tetraalkylammoniun ion $(C_nH_{2n+1})_4N^+$ has a 100% efficiency for the transfer from the charged liquid droplets into the gas phase. It was found that a cross check of the samples gave excellent agreement for the relative ion intensities of $(C_nH_{2n+1})_4N^+$ ions.

RESULTS AND DISCUSSION

Triply charged metal ion sugar complexes

In order to obtain information on the speciation of triply charged metal ions in solution, all combinations of the metal ions of Sc^{3+}, Y^{3+}, La^{3+}, Ce^{3+}, and Yb^{3+} and the sugar samples glucose, sucrose, raffinose, and α-cyclodextrin were examined. The electronic structures of the metal atoms are: $Sc(Ar3d^14s^2)$; $Y(Kr4d^15s^2)$; $La(Xe5d^16s^2)$; $Ce(Xe4f^15d^16s^2)$ and $Yb(Xe4f^146s^2)$. The ionization energies (eV) of doubly charged metal ions are $Sc^{2+}(24.8)$, $Y^{2+}(20.5)$, $La^{2+}(19.2)$, $Ce^{2+}(20.2)$, and $Yb^{2+}(25.2)$.

Figure 1 shows the electrospray mass spectrum for a H_2O/CH_3OH (1:1, v/v) solution of 10^{-5} M $LaCl_3$ and 5×10^{-4} M sucrose. A strong appearance of the series of La^{3+}(sucrose)$_n$ with $n \geq 3$, in addition to weaker La^{2+}(sucrose)$_n$ with

n = 1–3, is observed. Mixed cluster ions La^{3+}(sucrose)$_n(H_2O)_x(CH_3OH)_y$ were negligible. This suggests that the La^{3+} ion is more strongly solvated by the sucrose ligands than by the H_2O or CH_3OH ligands. This is likely to be due to the multidentate interaction of La^{3+} with sugar ligands.[11]

For all the H_2O/CH_3OH (1:1, v/v) solutions of M^{3+} and sugars, no cluster ions $M^{3+}(H_2O)_x(CH_3OH)_y$ were observed although strong signals of the cluster ions $MOH^{2+}(H_2O)_n$ appeared (the Sc^{3+} ion is exceptional and neither $Sc^{3+}(H_2O)_x(CH_3OH)_y$ nor $ScOH^{2+}(H_2O)_x(CH_3OH)_y$ ions could be detected). The absence of the cluster ions $M^{3+}(H_2O)_n$ and instead a strong appearance of $MOH^{2+}(H_2O)_n$ suggest that the ions $M^{3+}(H_2O)_n$ formed by the electrospray or laser spray experience the intramolecular proton transfer reaction through the formation of salt-bridge intermediate,[6] $MOH^{2+}(H_3O^+)(H_2O)_{n-2}$, which is followed by a Coulomb explosion to form $MOH^{2+}(H_2O)_{n-1-x}$.

$$M^{3+}(H_2O)_n \rightarrow MOH^{2+}(H_3O^+)(H_2O)_{n-2} \rightarrow$$
$$MOH^{2+}(H_2O)_{n-2-x} + H_3O^+(H_2O)_x$$
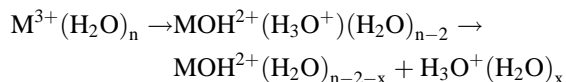
It is interesting to note that for all the metal ions studied (except for Sc^{3+}), the cluster ions $MOH^{2+}(H_2O)_n$ were found to be dominant and those composed of the mixed ligands $MOH^{2+}(H_2O)_x(CH_3OH)_y$(sugar)$_z$ were barely observed. This may be due to the fact that the interaction of the MOH^{2+} ion with H_2O is stronger than with CH_3OH or sugar ligands (see the latter part of this section).

Figure 2 displays the electrospray mass spectrum for a H_2O/CH_3OH (1:1, v/v) solution of 10^{-5} M $YbCl_3$ and 5×10^{-4} M raffinose. The cluster ions of Yb^{3+}(raffinose)$_n$ and Yb^{2+}(raffinose)$_n$ are strongly observed. Compared with
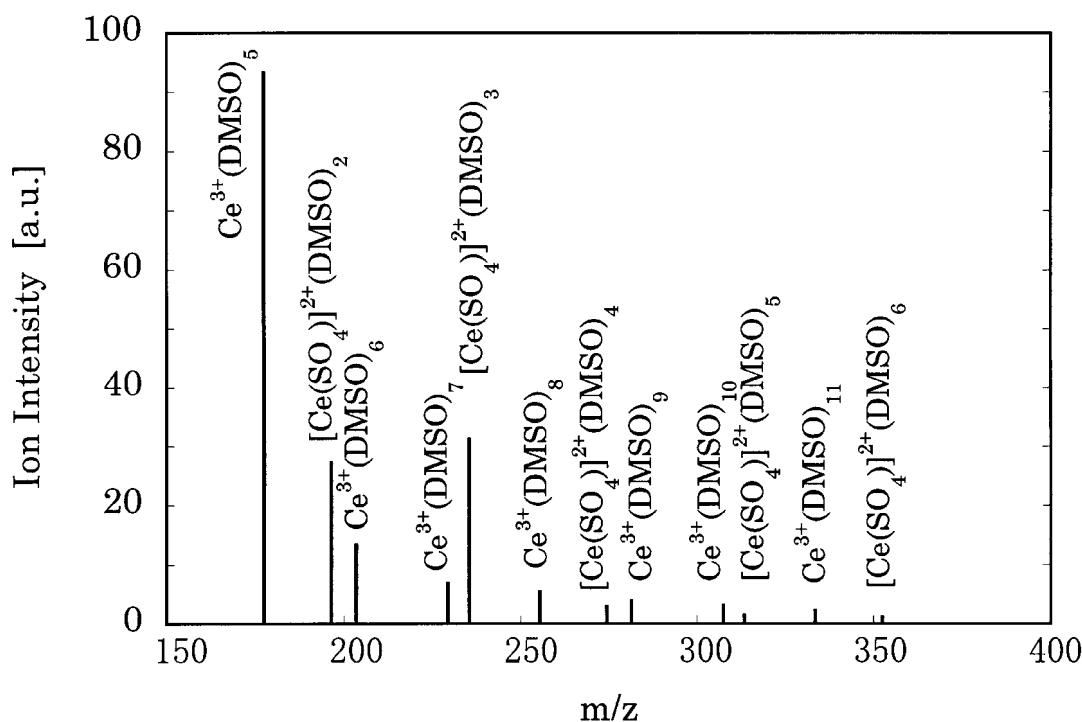
Figure 8. Laser spray mass spectrum for an aqueous solution of 10^{-4} M $Ce(SO_4)_2$ and 2×10^{-2} M DMSO. The transmission efficiencies of the quadrupole mass spectrometer were taken into consideration.

Fig. 1, the doubly charged metal cluster ions $Yb^{2+}(raffinose)_n$ appear much stronger and they are comparable to $Yb^{3+}(raffinose)_n$. This indicates that the intracluster charge-transfer reaction followed by a Coulomb explosion takes place to a greater extent than in the case of $La^{3+}(sucrose)_n$.

$$Yb^{3+}(raffinose)_n \rightarrow Yb^{2+}(raffinose^+)(raffinose)_{n-1} \rightarrow$$

$$Yb^{2+}(raffinose)_{n-1-x} + (raffinose)_{x+1}{}^+$$
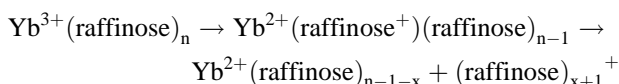
This is reasonable because the ionization energy of Yb^{2+} (25.2eV) is considerably higher than that of La^{2+} (19.2 eV). Here again, cluster ions $Yb^{3+}(sugar)_n$ and $Yb^{2+}(sugar)_n$ solvated by H_2O or CH_3OH ligands were negligible. It seems that the core metal ions Yb^{3+} and Yb^{2+} are well stabilized by the interaction with sugar ligands and the competitive solvation by protic solvents H_2O or CH_3OH is energetically less favorable.

Figure 3 shows the electrospray mass spectrum for a H_2O/CH_3OH (1:1, v/v) solution of 10^{-5} M $CeCl_3$ and 5×10^{-4} M α-cyclodextrin. $Ce^{2+}(\alpha$-cyclodextrin$)_n$ is found to be stronger than $Ce^{3+}(\alpha$-cyclodextrin$)_n$. There is a general trend that the triply charged metal ions are more easily reduced to doubly charged ions when cyclodextrins (for all of α-, β-, and γ-cyclodextrin and also for glucose) are used as ligands. The hydrophilic sites of cyclodextrin locate outside of the ring. In the complex of M^{3+} with cyclodextrin, the multidentate interaction may be more restricted compared to other oligosaccharides due to the rigid (i.e., non-flexible) structure of the ring-shaped cyclodextrin molecule. Thus the interactions of metal ions with cyclodextrins may be weaker than with more flexible oligosaccharides. The longer distances of the bonds between M^{3+} and ligands for weaker complexes may result in a decrease in the Coulomb barrier leading to the more efficient intramolecular charge-transfer reactions in the complex $M^{3+}(sugar)_n$ to form $M^{2+}(sugar)_n$.

In this work, glucose, sucrose, raffinose, and α-cyclodextrin were used as sugar samples. The intensities of the observed $M^{3+}(sugar)_n$ signals are roughly in the order, glucose $\approx$ α-cyclodextrin $<$ sucrose $<$ raffinose. The larger oligosaccharides (except for cyclodextrin) seem to form more stable metal cluster ions. The minimum numbers of n (n_{min}) for the observed cluster ions $M^{3+}(sugar)_n$ were found to decrease in the order, glucose $\rightarrow$ sucrose $\rightarrow$ raffinose. For example, the n_{min} values for $La^{3+}(sugar)_n$ are 5, 3 and 1 for glucose, sucrose, and raffinose, respectively. The multidentate interactions between M^{3+} ions and oligosaccharides seem to be enhanced with the molecular size.

For the combinations of the triply charged metal ions and sugar samples dealt with in this work, all the cluster ions $M^{3+}(sugar)_n$ could be observed except for $Sc^{3+}(sugar)_n$, for all sugars, and $Yb^{3+}(glucose)_n$. The difficulty with the observation of $Sc^{3+}(sugar)_n$ may be due to the small-size Sc^{3+} (0.88 Å) and the high ionization energy of Sc^{2+} ((24.8eV) which lead to the facile reduction of Sc^{3+} in the cluster ions. The absence of $Yb^{3+}(glucose)_n$ may also be partly due to the high ionization energy of $Yb^{2+}(25.2eV)$.

As the triply charged metal ions are found to form stable complexes with sugar molecules, the study was extended to the glycoside sample. Figure 4 displays the electrospray mass spectrum for a H_2O/CH_3OH(1:1, v/v) solution of 10^{-4} M $LaCl_3$, 10^{-4} M $NaCl$, and 10^{-4} M ginsenoside Rb_1. Since ginsenoside Rb_1 has two glucose-glucose groups at both terminal ends, a ginsenoside Rb_1 molecule attached by two La^{3+} ions may be expected to appear. However, as shown in Fig. 4, only the $La^{3+}($ginsenoside $Rb_1)$ ion could be observed in addition to the stronger $Na^+($ginsenoside $Rb_1)$ and $Na_2{}^{2+}($ginsenoside $Rb_1)$ ions. The absence of $(La^{3+})_2($ginsenoside $Rb_1)$ may be due to the destabilization caused by Coulomb repulsion between two La^{3+} ions. We think that multiply cationized molecules may be observed for larger size glycosides, glycoproteins, glycolipids, etc. A further study is now in progress in this respect.
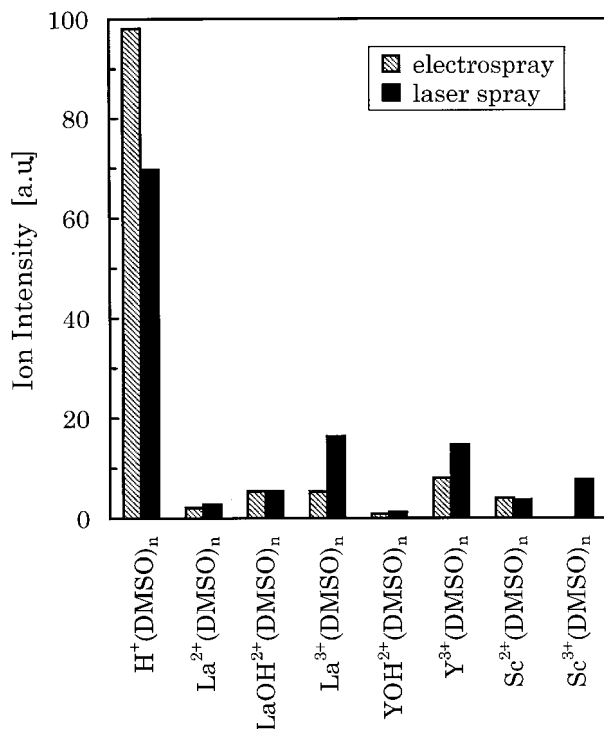
Figure 9. Intensities for all ions observed by laser spray and electrospray for a H_2O/CH_3OH (1:1, v/v) solution of mixed samples of 5×10^{-6} M $ScCl_3$, YCl_3, $LaCl_3$ and 2×10^{-2} M DMSO. The intensity of ion $(DMSO)_n$ corresponds to the value summed up for all n observed. The transmission efficiencies of the quadrupole mass spectrometer were taken into consideration.

In Figs 1–4 the peaks of $MOH^{2+}(H_2O)_n$ and other ions due to impurities (mainly NH_4^+) have been eliminated for the clarity of the spectrum. Figure 5 shows the intensities of all ions observed for a H_2O/CH_3OH (1:1, v/v) solution of 10^{-5} M $LaCl_3$ measured by electrospray as a function of sucrose concentration. Here, the intensity of ion(ligand)$_n$ corresponds to that summed up for all values of n. Gradual increases for $NH_4^+(H_2O)_n$ and $LaOH^{2+}(H_2O)_n$ with increase of sucrose concentration up to $\sim 5 \times 10^{-6}$ are seen in Fig. 5. This suggests that the efficiencies for the formation of gas phase ions from the charged liquid droplets are enhanced by the addition of sucrose (up to 10^{-5} M). With an increase of the sucrose concentration in solution, the network structure of the solvated ions in solution may be disturbed to a greater extent by the solute molecules added. This may decrease the hydration energies of ions in solution and thus increase the efficiency of the transfer of ions from solution to the gas phase.

To our surprise, the cluster ions of $NH_4^+(H_2O)_n$ and $LaOH^{2+}(H_2O)_n$ solvated by sucrose ligands are found to be negligible up to the highest sucrose concentration of 10^{-3} M. If the cluster ions $NH_4^+(H_2O)_n$ and $LaOH^{2+}(H_2O)_n$ were formed by the charged residue mechanism, a number of sucrose molecules must be present in the offspring droplets with $\geq 10^{-4}$ M^{12} and the cluster ions must be composed of many sucrose ligands (sucrose is nonvolatile). Apparently the charged residue model cannot explain the formation of gas phase $NH_4^+(H_2O)_n$ and $LaOH^{2+}(H_2O)_n$ ions for solutions of high sucrose concentration. It is highly likely that these ions are formed by the ion evaporation mechanism. This may be due to the higher surface activities of NH_4^+ and $LaOH^{2+}$ ions than of La^{3+} and La^{2+} ions.

The $La^{2+}(sucrose)_n$ starts to be observed at 10^{-7} M and shows a gradual increase up to $\sim 10^{-5}$ M. The mixed cluster ions $La^{2+}(sucrose)_n(H_2O)_x$ are negligible. This indicates that the La^{2+} ions formed by the charge reduction of La^{3+} are solvated predominantly by sucrose molecules in aqueous solution. This is a marked contrast that the $LaOH^{2+}$ ions solvated only by H_2O ligands are observed. It is worthwhile noting that the structures of the inner solvation shells for the solvated ions are highly specific on the kinds of the core ions and also of the ligands.

The $La^{3+}(sucrose)_n$ ions are observed with $\sim 5 \times 10^{-6}$ M and show a steep increase with $\geq 10^{-5}$ M. The decrease of $La^{2+}(sucrose)_n$ but the steady increase of $La^{3+}(sucrose)_n$ with $\geq 10^{-4}$ M indicate that the charge reduction $La^{3+} \rightarrow La^{2+}$ is being suppressed with increase of sucrose concentration.

The relative intensities of the $LaOH^{2+}(H_2O)_n$ ions with different n were found to be nearly independent of the sucrose concentration. The intensities of $LaOH^{2+}(H_2O)_n$ for respective n are roughly in the order n = 16 < 15 < 14 < 13 < 12 < 11 < 10 < 9 < 2 < 8 < 7 < 6 < 5 < 4 < 3. In contrast, the relative intensities of the $La^{3+}(sucrose)_n$ ions with different n show a marked dependence on the sucrose concentration. Figure 6 shows the intensities of $La^{3+}(sucrose)_n$ for all n observed as a function of sucrose concentration. It should be noted that the $La^{3+}(sucrose)_n$ ion with only n = 3 is observed at 5×10^{-6} and 10^{-5} M: The absence of smaller cluster ions $La^{3+}(sucrose)_n$ with n = 1 and 2 but only the appearance of $La^{3+}(sucrose)_3$ suggest that the La^{3+} ion is already solvated by three sucrose molecules in the liquid phase. This argument is supported by the crude calculation that the number of sucrose molecules in the third-generation offspring droplets with sucrose concentrations of 5×10^{-6} and 10^{-5} M are less than 0.1.[12] This is also supported by the observation of Petrucci and co-workers[13] that the multiply charged metal ions form stable complexes with carbohydrates in aqueous solution.

Figure 6 shows the appearance and rapid growth of cluster ions with larger n (n $\geq$ 3) with sucrose concentrations $\geq 5 \times 10^{-5}$ M. Similar results have also been reported for the formation of alkali metal cluster ions[14] and protonated arginine clusters[15] with an increase of the sample concentration. The cluster ions $La^{3+}(sugar)_n$ up to n = 10, are observed. These results may be rationalized by the charged residue model.[12] Due to solvent evaporation and droplet shrinkage the nonvolatile solute (sucrose) concentration may undergo a large increase in offspring droplets. The charged droplets prone to uneven fission give approximately 20 smaller droplets at the Rayleigh instability limit[16] and these offspring droplets may in turn produce third-generation droplets when the Rayleigh instability limit is again reached.[12] An increase in nonvolatile solute concentration by a factor of 140 may be expected after three such uneven events, eventually leading to the formation of cluster ions.[12] Figure 6 shows the intensities of $La^{3+}(sucrose)_n$, with n = 9 and 10, increasing by a factor of ~ 10 with an increase of the sucrose concentration from 10^{-4} to 10^{-3} M. This suggests that the formation of these cluster ions are reasonably explained by the charged residue model. Because the mass range of the quadrupole mass spectrometer used in the present experiment is limited to m/z 1100, the measurement of the cluster ions $La^{3+}(sucrose)_n$ with n $\geq$ 11 was not possible Considering that $La^{3+}(sucrose)_{10}$ is the strongest of $La^{3+}(sucrose)_n$ at 10^{-3}

M, the cluster ions with $n \geq 11$ may also be present at this sucrose concentration.

In summary, the ion evaporation mechanism must be invoked to explain the transfer of more surface active ions in solution to the gas phase, while the transfer of low surface active ions may be explained by the charged residue model.

Triply charged metal ion DMSO and HMPA complexes

Kebarle and co-workers[7] observed abundant triply charged metal ion clusters, $M^{3+}(ligand)_n$, for M = Y, La, Ce, Nd, and Sm and the ligands dimethylsulfoxide (DMSO) and dimethylformamide by electrospray. They did not detect the Sc^{3+} cluster ions. However, strong cluster ions $Sc^{3+}(DMSO)_n$ could be observed in the present study by electrospray and laser spray. Figure 7 displays the laser spray mass spectrum for an aqueous solution of 10^{-5} M $ScCl_3$ and 2×10^{-1} M DMSO. Series of $Sc^{3+}(DMSO)_n$ ions are observed as major ions. No $ScOH_2^+$ ion and its clusters were observed under any experimental conditions as in the case for the solution of Sc^{3+} and sugar samples. The appearance of much stronger signals for $Sc^{3+}(DMSO)_n$ than for $Sc^{3+}(DMSO)_n$ in Fig. 7 clearly indicates the presence of the appreciable energy barrier for the intracluster charge transfer reaction in $Sc^{3+}(DMSO)_n$ despite the fact that the ionization energy of DMSO (9.01 eV) is considerably lower than that of Sc^{2+} (24.8 eV) and the gas phase charge transfer reaction, $Sc^{3+} + DMSO \rightarrow Sc^{2+} + DMSO^+$, is as much as 15.8 eV exoergic. It is likely that the bond distances between M^{3+} and DMSO ligands are so close that the intracluster charge transfer reaction becomes endoergic due to Coulomb repulsion between M^{2+} and $DMSO^+$ in the complex. In Fig. 7, $Sc^{3+}(DMSO)_n$ clusters up to n = 15 are observed. If some DMSO ligands locate in the second or outer shells and are separated from the core Sc^{3+} ion long enough, the tunneling charge transfer between Sc^{3+} and outer DMSO would become exoergic. Nonoccurrence of the intracluster charge transfer in $Sc^{3+}(DMSO)_n$ up to n = 15 may mean that the charge-transfer reaction is suppressed due to the extensive charge stabilization of Sc^{3+} by the cooperative solvation of highly polarized first-shell DMSO ligands.

For all the triply charged metal ions M^{3+} used in this work (M = Sc, Y, La, Ce, and Yb), abundant $M^{3+}(DMSO)_n$ cluster ions could be observed. Hexamethylphosphoramide (HMPA) was also examined as ligand to observe the triply charged metal ion clusters. Although strong signals of the cluster ions $M^{3+}(HMPA)_n$ for M = Y, La, and Ce were observed, those for Sc^{3+} and Yb^{3+} could not be detected. Generally speaking, DMSO seems to be one of the best ligands for the observation of multiply charged metal ions.

We also made some effort to observe the gas phase Ce^{4+} ion clusters. Figure 8 displays the laser spray mass spectrum for an aqueous solution of 10^{-4} M $Ce(SO_4)_2$ and 2×10^{-2} M DMSO. The strong appearance of $Ce^{3+}(DMSO)_n$ and $[Ce(SO_4)]^{2+}(DMSO)_n$ was observed but no $Ce^{4+}(DMSO)_n$ could be detected. This result is reasonable because Ce^{3+} has a very high ionization energy (36.7 eV). When the concentration of $Ce(SO_4)_2$ was decreased to 10^{-5} M, the $[Ce(SO_4)]^{2+}(DMSO)_n$ ions became almost negligible although a strong $Ce^{3+}(DMSO)_n$ was still observed. The fact that the ion $Ce(SO_4)^{2+}(DMSO)_n$ is observed only for the higher concentration of $Ce_2(SO_4)_2$ indicates that this ion is formed by the recombination of Ce^{4+} and SO_4^{2-} in the charged liquid droplets. The charge reduction of Ce^{4+} in the cluster $CeSO_4^{2+}(DMSO)_n$ is suppressed by the ionic bond formed between Ce^{4+} and SO_4^{2-}.

Comparative study of laser spray and electrospray

In order to investigate the characteristics of the laser spray developed in our laboratory,[10] a comparative study of laser spray and electrospray was performed using H_2O/CH_3OH (1:1, v/v) solutions of mixed samples of 5×10^{-6} M $ScCl_3$, YCl_3, and $LaCl_3$ and 2×10^{-2} M DMSO. Figure 9 summarizes the intensities for all ions observed by laser spray and electrospray. Here the intensity of ion $(DMSO)_n$ corresponds to the value summed up for all n taking into consideration the transmission efficiency of the quadrupole mass spectrometer. In general, laser spray gives stronger intensities for the metal ion clusters than electrospray. The outstanding difference is that the cluster ions $Sc^{3+}(DMSO)_n$ could not be detected by electrospray while strong signals of these cluster ions were obtained by laser spray. In contrast, the intensities of $H^+(DMSO)_n$ measured by electrospray are stronger than those by laser spray. Because the size of Sc^{3+} is the smallest of the three metal ions studied (Sc^{3+}, Y^{3+} and La^{3+}), Sc^{3+} may have the least efficiency for the formation of gas phase ions from the liquid phase due to its large solvation energy. On the other hand, the $H^+(DMSO)_2$ must be the easiest to transfer from the liquid to the gas phase because the protic H atom is sandwiched by two hydrophobic DMSO molecules, $(CH_3)_2SO \cdots H^+ \cdots OS(CH_3)_2$. Figure 9 clearly indicates that laser spray is more suitable for the detection of ions with low surface activities. This merit of laser spray may be due to the ability of the formation of finer and more highly charged liquid droplets. A further study on the mechanisms for the formation of gas phase ions by laser spray is in progress in our laboratory.

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