Chemical Reactions Involving Multi-Solvated Electrons on Liquid Beam Surface of CaI_2 Alcohol Solutions

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Received: December 31, 2000; In Final Form: March 9, 2001

A continuous liquid flow (a liquid beam) of a calcium iodide (CaI_2) solution in ethanol (EtOH) in a vacuum was irradiated with a UV laser at different wavelengths and powers. Product ions ejected from the solution surface following multiphoton excitation via the charge-transfer-to-solvent (CTTS) band of I^- were analyzed by a time-of-flight mass spectrometer. Under irradiation of the laser at a weak power, solvated cluster ions $CaOEt^+$ $(EtOH)_m$ ($m = 0-6$), $CaOH^+$ $(EtOH)_m$ ($m = 0-1$), and CaI^+ $(EtOH)_m$ ($m = 0-6$) (Class I) were found to be produced, whereas at an intense power, cluster ions containing neutral salts, $[Ca_n(OEt)_i(OH)_j(O)_k(I)_l]^+$ (Class II), were produced additionally. The relative abundances of the cluster ions of Class II increased as the irradiation laser power increased. The abundance was particularly high when the excitation laser was resonant to the CTTS band. It was concluded that more than one solvated electrons participate in the production of the Class II cluster ions.

1. Introduction

A variety of reactions involving solvated electrons has been investigated intensively and extensively in a liquid phase, and even their rate constants have been measured by use of pulse radiolysis, as exemplified in one-electron capture by O_2 into O_2^- and dissociative one-electron capture by ROH (alcohol) into $RO^- + H$.[1,2] Similar reactions have been investigated by laser photoexcitation, where a solvated electron is produced by excitation of the charge-transfer-to-solvent (CTTS) band of a negative ion in a solution.[3] The formation of RO^- is also observed in the reaction of ROH with a photoproduced solvated electron.[4] This photoinduced method is practically sensible to a study on the ultrafast dynamics of a reaction involving a solvated electron.[5−7] On the other hand, reactions of solvated electrons on liquid surfaces have been investigated by use of a continuous liquid flow in a vacuum (liquid beam), combined with multiphoton ionization−mass spectrometry.[8−10] Solvated electrons on the solution surfaces are produced by excitation of the charge-transfer-to-solvent (CTTS) band of the solute halides on the solution surfaces, and ionic species formed and ejected from the liquid surface are analyzed by mass spectrometry. It has been found that in a CaI_2 solution in ethanol (EtOH), a single solvated electron liberated from an excited I^- in the solution react with EtOH into EtO^- and Ca^{2+} into Ca^+.

As described above, almost all the reactions reported so far are those involving a single solvated electron throughout the reactions because the solvated-electron density is too low to proceed via a reaction in which more than one solvated electrons take part. If this is the case, we can expect that more novel reaction products result through the reduction of chemical species appearing in the course of the reaction by the additional solvated electrons. A dimerization reaction of solvated electrons in an aqueous solution is one of the simplest and the most elementary reactions of this kind

$$e_s^- + e_s^- + 2H_2O \rightarrow H_2 + 2OH^- \qquad (1)$$

which is often encountered in radiolysis processes. Obviously, the dimerization reaction is a second-order reaction with respect to the solvated-electron density, of which rate constant is measured by several groups.[11−15] One can investigate such novel reactions occurring in a solution by observing reaction processes induced by an intense laser light at it because many solvated electrons are generated by the irradiation. In the present study, we explored ion−molecule reactions on a liquid beam of a CaI_2 solution in ethanol under irradiation of an intense UV laser (220−250 nm). In particular, chemical reactions involving more than one solvated electrons were found to proceed very efficiently when the wavelength of the intense laser is resonant to the CTTS band of I^- in the solution; solvated electrons are generated most efficiently at the resonant condition. The product ions were compared with those produced by irradiation of a 250 nm laser, which is off-resonant to the CTTS band.

2. Experimental Section

The apparatus employed in the present experiment has been described in detail previously[16−18] so that only its overview relevant only to the present experiment was shown in more detail. A liquid beam (continuous laminar liquid flow) of an ethanol solution of CaI_2 was introduced into a source chamber from a nozzle having an aperture with 20 μm in diameter, supplied by a Shimadzu LC-6A pump designed for a liquid chromatograph. The flow rate was maintained at 0.2 mL/min with a pressure of typically 20 atm inside the nozzle. The source chamber was evacuated by a 1200 L s^{-1} diffusion pump and a liquid N_2 trap down to $10^{-6}-10^{-5}$ Torr during injection of the liquid beam. The solution was prepared from commercially available ethanol and CaI_2 (n hydrate, > 99.5%). Insoluble impurity particles in the CaI_2−ethanol solution were removed by filtration to prevent the nozzle from being clogged.

The liquid beam was crossed at 2 mm downstream from the nozzle with a UV laser (220−250 nm) in the first acceleration

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10.1021/jp0046288 CCC: $20.00

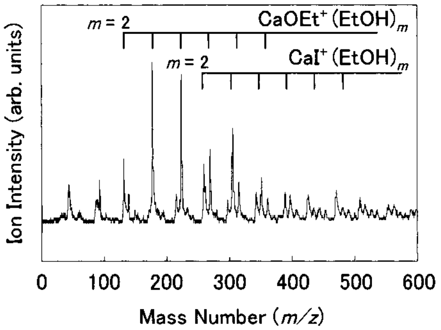


Figure 1. Mass spectrum of ions produced by irradiation of a 220 nm laser on the liquid beam of a 0.5 M CaI_2 solution in ethanol. The power of the laser is 60 μJ/pulse. Cluster ions, $CaOEt^+$ $(EtOH)_m$ and CaI^+ $(EtOH)_m$, are observed. These cluster ions belong to Class I.

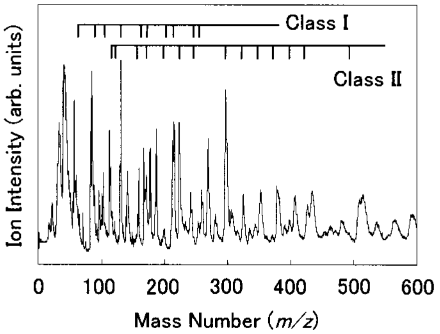


Figure 2. Mass spectrum of ions produced by irradiation of a 220 nm laser on the liquid beam of a 0.5 M CaI_2 solution in ethanol. The power of the laser is 130 μJ/pulse. Ions, CaX^+ $(EtOH)_m$ (X = OEt, OH, and I) (Class I) and $[Ca_n(OEt)_i(OH)_j(O)_k(I)_l]^+$ (Class II) are recognizable.

region of the TOF mass spectrometer. The laser was obtained by frequency-doubling the output of a Quanta-ray PDL-3 dye laser pumped by the third harmonics of a Quanta-ray GCR-3 Nd:YAG laser. The laser was tightly focused onto the liquid beam by a lens with a focal length of 450 mm. The laser power (50−400 μJ/pulse) was monitored by a LAS PM-200 energy meter. The fluence of the laser was 160−1300 mJ $pulse^{-1}$ cm^{-2}, where the laser was focused into ~0.2 mm in diameter.

A reflectron TOF mass spectrometer was employed for analyzing the mass-to-charge ratios, m/z, of ions from the liquid beam as follows: Ions ejected from the liquid beam by photoexcitation of the UV laser irradiation were accelerated by a pulsed electric field in the acceleration region in the direction perpendicular to both the liquid and the laser beams after a time delay (~1 μs) from the photoexcitation. The ions were then steered and focused by a set of vertical and horizontal deflectors and an einzel lens. Traveling in a 1.5-m field-free flight tube, the ions were reversed by a reflectron which provides a reversing field tilted by 2° off the beam axis. A train of spatially mass-selected ions were detected after travelling another 0.5-m field-free region by a Murata EMS-6081B Ceratron electron multiplier. Signals from the multiplier were amplified and processed by a Yokogawa DL 1200E digital oscilloscope based on an NEC 9801 microcomputer. The mass resolution, defined as $m/\Delta m$, was typically 200 at a typical experimental condition.

3. Results

Figures 1 and 2 show mass spectra of ions produced by irradiation of a 220 nm laser on a liquid beam of a 0.5 M CaI_2 solution in ethanol at 60 and 130 μJ/pulse, respectively. Peaks in the mass spectrum shown in Figure 1 are assigned to cluster ions $CaOEt^+$ $(EtOH)_m$ ($m = 0-6$), $CaOH^+$ $(EtOH)_m$ ($m = 0-2$), and CaI^+ $(EtOH)_m$ ($m = 0-5$), which will be categorized as Class I hereafter. With an increase in the laser power, ions beside the cluster ions of Class I gain more intensity, as shown in Figure 2. The mass numbers of the ions are given by $40n + 45i + 17j + 16k + 127l$ (n = 2, 3, ..., and i, j, k, and l = 0, 1, 2, ..., with the constraint of $2n - i - j - 2k - l = 1$); 40, 45, 17, 16, and 127 correspond to the masses of Ca^{2+}, EtO^-, OH^-, O^{2-}, and I^-, respectively. The constraint, $2n - i - j - 2k - l = 1$, implies that these ions are singly charged. These ions are assigned to $[Ca_n(OEt)_i(OH)_j(O)_k(I)_l]^+$, and are categorized as Class II hereafter.

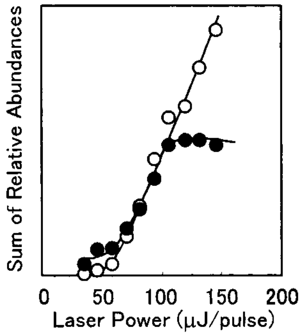


Figure 3. Dependence of the sum of the relative abundances on the laser power; solid and open circles represent Class I (CaX^+ $(EtOH)_m$ (X = OEt, OH, and I)) and Class II ($[Ca_n(OEt)_i(OH)_j(O)_k(I)_l]^+$) cluster ions, respectively.

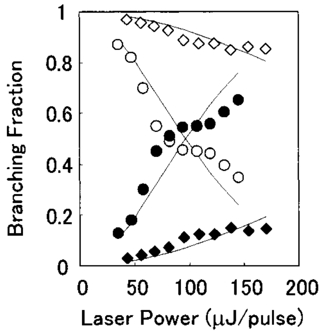


Figure 4. Branching fractions of Class I (○) and Class II (●) cluster ions as a function of the laser power at 220 nm and those of Class I (◇) and Class II (◆) at 250 nm. Class I: CaX^+ $(EtOH)_m$ (X = OEt, OH, and I). Class II: $[Ca_n(OEt)_i(OH)_j(O)_k(I)_l]^+$. The solid curves represent the calculated dependences by using eqs 9 and 10 (see text).

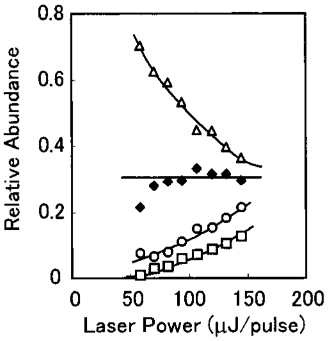


Figure 5. Relative abundances of EtO^- (△), OH^-(○), O^{2-} (□), and I^- (◇) contained in all the Class II cluster ions observed are compared with the calculated ones by using eqs 1−4.

Figure 3 shows the laser-power dependence of the sum of the relative abundances of the Class I and that of the Class II cluster ions under irradiation of the 220 nm laser. The abundance of the Class I cluster ions increases and then levels off, whereas that of the Class II cluster ions continues to increase as the laser power increases. Figure 4 shows the laser-power dependences of the relative abundances of the cluster ions of Class I and Class II under irradiation of the 220 and 250 nm lasers. The branching fraction for the production of the Class I cluster ions decreases, whereas that of the Class II cluster ions increases with an increase in the laser power both at 220 and 250 nm. This tendency is the most prominent when the excitation laser is resonant to the CTTS band (220 nm).

Figure 5 shows the relative abundance, R_X, of a cluster ion containing X (X = EtO^-, OH^-, O^{2-}, and I^-), which belongs to Class II. As shown below, R_X is defined as

$$R_{EtO^-} = \frac{\sum_i iI_{i,j,k,l}}{\sum_i iI_{i,j,k,l} + \sum_j jI_{i,j,k,l}\sum_k kI_{i,j,k,l} + \sum_l lI_{i,j,k,l}} \quad (1)$$

$$R_{OH^-} = \frac{\sum_j jI_{i,j,k,l}}{\sum_i iI_{i,j,k,l} + \sum_j jI_{i,j,k,l}\sum_k kI_{i,j,k,l} + \sum_l lI_{i,j,k,l}} \quad (2)$$

$$R_{O^{2-}} = \frac{\sum_k kI_{i,j,k,l}}{\sum_i iI_{i,j,k,l} + \sum_j jI_{i,j,k,l}\sum_k kI_{i,j,k,l} + \sum_l lI_{i,j,k,l}} \quad (3)$$

$$R_{I^-} = \frac{\sum_l lI_{i,j,k,l}}{\sum_i iI_{i,j,k,l} + \sum_j jI_{i,j,k,l}\sum_k kI_{i,j,k,l} + \sum_l lI_{i,j,k,l}} \quad (4)$$

where $I_{i,j,k,l}$ designates the intensity of $[Ca_n(OEt)_i(OH)_j(O)_k(I)_l]^+$. As the laser power increases, R_{EtO^-} decreases monotonically, R_{OH^-} and R_{O2^-} increase, and R_{I^-} is practically unchanged.

4. Discussion

4.1. Ion-Ejection from Liquid Beam. In comparison with our previous results, the following processes are conceivable: A solute calcium iodide, CaI_2, in an ethanol solution is dissociated into CaI^+ and I^- and further into Ca^{2+} and $2I^-$. A solvated electron is produced in the solution by photoexcitation of the charge-transfer-to-solvent (CTTS) band of I^-, having the absorption maximum at 220 nm. It is highly likely that the solvated electron in the vicinity of the liquid beam surface absorbs one more photon and is then liberated from the liquid beam surface because the photon energy (5.6 eV) exceeds the binding energy of the solvated electron (less than 2.9 eV [19]). As a result, the surface region of the liquid beam becomes positively charged, so any cation in this region is ready for ejection due to Coulomb repulsion by neighboring positive charges. The positive ions in the surface region are considered to be Ca^+, $CaOEt^+$, CaI^+, and H^+, which are generated by various reaction processes in the solution, as discussed in the following section. These ions are ejected with several accompanying ethanol molecules from the liquid surface.[20,21] The nascent cluster ion thus produced releases several solvent molecules (evaporative cooling) as they travel in the gas phase because of their rich internal energy accumulated through a geminate recombination cycle of the solvated electron and I radical.[22] Formation of the nascent cluster ion and its evaporative cooling are expressed as

$$X^+ \text{ (sol)} \rightarrow X^+ \text{ (EtOH)}_n \text{ (g)} \quad (5)$$

$$X^+ \text{ (EtOH)}_n \text{ (g)} \rightarrow X^+ \text{ (EtOH)}_m \text{ (g)} + (n-m) \text{ EtOH} \quad (6)$$

where X^+ represents an ion produced in the solution and X^+ (g) represents X^+ in the gas phase.

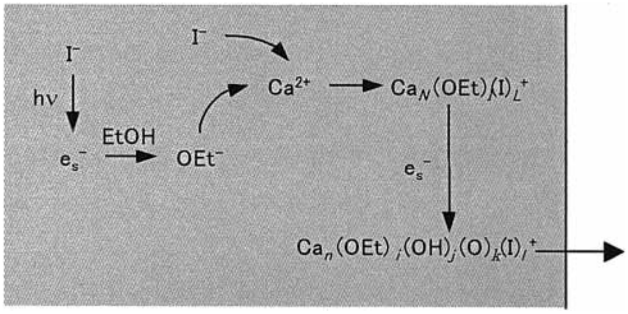
Studies on NaI (solvent)$_n$ in the gas phase show that a contact ion pair, Na^+I^-, has the A ← X absorption at 250 nm in H_2O and 270 nm in NH_3 clusters.[23,24] The 250 nm laser is likely to be resonant to the A ← X band of CaI_2 because (1) both CaI_2 and NaI consist of a metal cation and iodide anions (contact ion pair) and (2) CaI_2 is present as a contact ion pair on the surface of its ethanol solution, on the basis of our previous result that NaI aggregates on an ethanol-solution surface.[22]

4.2. First-Order Reactions of Solvated Electrons. One can explain the formation of a Class I cluster ion by consulting with our previous studies as follows:[14,15] A solvated electron produced by laser excitation of I^- reacts with EtOH into EtO^-, which further associates with Ca^{2+} to form $CaOEt^+$. The ion, $CaOH^+$, is produced similarly when OH^- is generated in the intermediate stage. One solvated electron is involved in these association reactions, and hence, the abundances of $CaOEt^+$ and $CaOH^+$ increase linearly with the number of the solvated electron (first-order reaction). Practically, no solvated electron is involved in the formation of CaI^+ because the electrolytic dissociation of CaI_2 in the solution provides a dominant amount of CaI^+. In addition to the $CaOEt^+$ formation by the association of Ca^{2+} with EtO^-, $CaOEt^+$ is produced by intracluster reactions in Ca^{2+} (EtOH)$_n$ after it is ejected in the gas phase, by dissociation of Ca^{2+} (EtOH)$_n$ into $CaOEt^+$ (EtOH)$_m$ and H^+ (EtOH)$_{m'}$,[14] and by unimolecular dissociation of Ca^+ (EtOH)$_n$ into $CaOEt^+$ (EtOH)$_m$.[15]

4.3. Higher-Order Reaction of Solvated Electron. As shown in Figure 2, the Class II cluster ions, $[Ca_n(OEt)_i(OH)_j(O)_k(I)_l]^+$, which are not present originally in the solution, are generated only when the liquid beam is irradiated by an intense laser. Evidently, many solvated electrons are involved in the formation of the Class II cluster ions because the Class II cluster ions contain more than one anion of OEt^-, OH^-, and O^{2-}, which are produced from one or more solvated electrons. In fact, the Class II cluster ions are most efficiently produced by resonant excitation of the CTTS band of I^- (∼220 nm) (see Figure 4). This behavior is consistent with the conjecture that more than one solvated electron is involved in this case. In nonresonant excitation, the abundance of the Class II cluster ions was found to be significantly reduced. The wavelength, 250 nm, is resonant to the A ← X excitation of a contact ion pair, $Ca^{2+}(I^-)_2$, on the solution surface but off-resonant to the CTTS band so that the solvated electrons are not generated efficiently. Accordingly, the Class II cluster ions are produced with a much less efficiency.

Figure 5 shows the relative abundances of EtO^-, OH^-, O^{2-}, and I^- contained in the Class II cluster ions as a function of the laser power. No substantial change of the I^- abundance with the laser power is consistent with the fact that I^- is always supplied from the dissociation of CaI_2. On the other hand, the relative abundance of EtO^- decreases, while those of OH^- and O^{2-} increase as the laser power increases. Radiolysis studies have revealed that EtO^- is the primary product of the reaction of a solvated electron with an ethanol molecule. Taking advantage of this result, one can conclude that the primary product of the present reaction is $[Ca_N(OEt)_I(I)_L]$, which reacts

SCHEME 1



further with solvated electrons into $[Ca_n(OEt)_i(OH)_j(O)_k(I)_l]$; that is

$$[\mathrm{Ca}_N(\mathrm{OEt})_I(\mathrm{I})_L]^+ \xrightarrow{e_s^-} [\mathrm{Ca}_n(\mathrm{OEt})_i(\mathrm{OH})_j(\mathrm{O})_k(\mathrm{I})_l]^+ \tag{7}$$

The processes of the cluster ion formation are summarized in Scheme 1.

There is a tendency that Ca^{2+} associates with EtO^- more preferentially than I^- because Ca^{2+} is a "hard" acid while EtO^- and I^- are "hard" and "soft" bases, respectively.[25] Note that a hard acid associates more readily with a hard base than with a soft base. On the basis of the affinity rule between an acid–base pair as described above, we propose the mechanism for the formation of the Class II cluster ions as follows: Let us assume that Ca^{2+} is surrounded by six I^-'s in the solution, as is the case of a CaI_2 crystal. It is conceivable that $[Ca_2(OEt)_2]^{2+}$ is generated when two I^-'s are replaced with two EtO^-'s in a neares-neighbor pair of Ca^{2+} because two interstitial I^-'s are separating the neighboring two Ca^{2+} ions. Similarly, $[Ca_3(OEt)_3]^{3+}$ is generated from a nearest-neighbor trio of Ca^{2+}'s by replacing three of the neighboring I^-'s with three EtO^-'s. These intermediate species should react with chemical species in its vicinity. For example, $[Ca_2(OEt)_2]^{2+}$ reacts with I^- into $[Ca_2(OEt)_2I]^+$, etc. We can extend this argument that the cluster ions containing n Ca^{2+} ions are produced when n of the six I^- ions are replaced with EtO^-. The probability, p, of the replacement of I^- with EtO^- is considered to be proportional to the laser power, I. Then the number of the Ca^{2+} ions contained in a given product ion follows a binomial distribution as

$$P(n) = \frac{6!}{n!(6-n)!}p^n(1-p)^{6-n} = \frac{6!}{n!(6-n)!}(kI)^n(1-kI)^{6-n} \tag{8}$$

where n is the number of Ca^{2+} ions in the product cluster ion, $P(n)$ is the relative abundance of the cluster ion, and k is equal to p/I, which represents the efficiency of the reactions involving the solvated electrons. In this equation, $P(0)$ represents no replacement of I^- with EtO^- to form Ca^{2+} $(EtOH)_N$ or CaI^+ $(EtOH)_N$, $P(1)$ represents the replacement of one I^- into one EtO^- to form $CaOEt^+$ $(EtOH)_N$, and $P(n>1)$ represents the replacement of n ions of I^- with EtO^- to form $[Ca_n(OEt)_n]^{n+}$ ($n > 1$). Both $P(0)$ and $P(1)$ contribute to the formation of the Class I cluster ions, and $P(n > 1)$ contributes to the formation of the Class II cluster ions. The relative abundances of the Class I and II cluster ions (R_I and R_{II}, respectively) are then given as

$$R_I = P(0) + P(1) \tag{9}$$

$$R_{II} = \sum_{n=2}^{6} P(n) \tag{10}$$

The curves in Figure 4 represent the fitting results of the relative abundance of the Class I and II cluster ions with eqs 9 and 10, respectively, with k as the fitting parameter. The model calculation reproduces the experimental results reasonably well. The obtained k values were 2.7 and 0.80 $(mJ/pulse)^{-1}$ for the 220 and 250 nm lasers, respectively. The 220 nm laser is about 3 times more efficient for the solvated electron production than the 250 nm laser because the k value of the 220 nm laser is about 3 times larger than that of the 250 nm laser.

5. Conclusion

Under irradiation of an intense laser at the wavelength resonant to the CTTS band, chemical reactions involving more than one solvated electrons were found to proceed on a surface of a CaI_2 ethanol solution. A much stronger interaction between a hard acid and a hard base ($Ca^{2+}\cdots EtO^-$) than that between a hard acid and a soft base ($Ca^{2+}\cdots I^-$) favors the formation of the Class II cluster ions, $[Ca_n(OEt)_i(OH)_j(O)_k(I)_l]^+$.

Acknowledgment. The authors are grateful to Mr. Yoshihiro Takeda for his assistance in the early stage of the liquid beam studies. This research was supported by the Special Cluster Research Project of Genesis Research Institute, Inc.

References and Notes

(1) In *Radiation Chemistry*; Faehataziz, Rodgers, M. A. J., Eds.; VCH: New York, 1987.

(2) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

(3) Blandamer, M. J.; Fox, M. F. *Chem. Rev.* **1970**, *70*, 59.

(4) Kenney-Wallace, G. A.; Hall, G. E.; Hunt, L. A.; Sarantidis, K. *J. Phys. Chem.* **1980**, *84*, 1145.

(5) Silva, C.; Walhout, P. K.; Reid, P. J.; Barbara, P. F. *J. Phys. Chem. A* **1998**, *102*, 5701.

(6) Silva, C.; Walhout, P. K.; Yokoyama, K.; Barbara, P. F. *Phys. Rev. Lett.* **1998**, *80*, 1086.

(7) Kloepfer, J. A.; Vilhiz, V. H.; Lenchenkov, V. A.; Bradforth, S. E. *Chem. Phys. Lett.* **1998**, *298*, 120.

(8) Matsumura, H.; Mafuné, F.; Kondow, T. *J. Phys. Chem.* **1995**, *99*, 5861.

(9) Kohno, J.; Mafuné, F.; Kondow, T. *J. Phys. Chem. A* **1999**, *103*, 1518.

(10) Kohno, J.; Mafuné, F.; Kondow, T. *J. Phys. Chem. A* **2000**, *104*, 1079.

(11) Christensen, H.; Sehested, K. *J. Phys. Chem.* **1986**, *90*, 186.

(12) Boyle, J. W.; Ghormley, J. A.; Hochauadel, C. J.; Riley, J. F. *J. Phys. Chem.* **1969**, *75*, 2886.

(13) Matheson, M. S.; Rabani, J. *J. Phys. Chem.* **1965**, *69*, 1324.

(14) Hickel, B.; Sehested, K. *J. Phys. Chem.* **1985**, *89*, 5271.

(15) Tesler, Th.; Schindewolf, U. *J. Phys. Chem.* **1986**, *90*, 5378.

(16) Mafuné, F.; Takeda, Y.; Nagata, T.; Kondow, T. *Chem. Phys. Lett.* **1992**, *119*, 615.

(17) Mafuné, F.; Takeda, Y.; Nagata, T.; Kondow, T. *Chem, Phys. Lett.* **1994**, *216*, 234.

(18) Mafuné, F.;. Kohno, J.; Nagata, T.; Kondow, T. *Chem, Phys. Lett.* **1994**, *218*, 7.

(19) The binding energy of a solvated electron in an ethanol solution should be less the binding energy of a hydrated electron (∼2.9 eV^2) because water molecules bind more tightly than ethanol molecules to a solvated electron because of the larger dipole moment of water than ethanol.

(20) Mafuné, F.; Kohno, J.; Kondow, T. *J. Chin. Chem. Soc.* **1995**, *42*, 449.

(21) Mafuné, F.; Kohno, J.; Kondow, T. *J. Phys. Chem. A* **2000**, *104*, 243.

(22) Matsumura, H.; Mafuné, F.; Kondow, T. *J. Phys. Chem. B* **1999**, *103*, 838.

(23) Grégoire, G.; Mons, M.; Dimicoli, I.; Dedonder-Lardeux, C.; Jouvet, C.; Martrenchard, S.; Solgadi, D. *J. Chem. Phys.* **2000**, *112*, 8794.

(24) Dedonder-Lardeux, C.; Grégoire, G.; Jouvet, C.; Martrenchard, S.; Solgadi, D. *Chem. Rev.* **2000**, *100*, 4023.

(25) Pearson, R. G. *J. Chem. Education* **1968,** *45*, 581.