First Observation of Electron Paired with Divalent and Trivalent Nonreactive Metal Cations in Water

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The effects of several chloride and perchlorate salts (NH_4^+, Na^+, Mg^{2+}, Tb^{3+}) at high concentration in water on the optical absorption spectrum of the hydrated electron are studied. For a given salt, the hydrated electron spectrum shifts toward high energy as the salt concentration is increased. For the same chloride salt concentration, the blue shift of the hydrated electron spectrum increases with the charge of the cation, the largest corresponding to the pair formed with Tb^{3+}, studied for the first time.

Introduction

Observed in water by pulse radiolysis and transient optical absorption measurements in 1962,[1] the solvated electron can be formed in a variety of solvents and has been intensively studied during the past decades. Since the 1970s the absorption spectrum of the solvated electron was measured in different solvents like amines, ethers, and alcohols.[2] However, due to the importance of water in physics, chemistry, and biochemistry, the solvated electron in water has attracted much interest in order to determine its structure in the ground and excited states. Several quantum simulations of the hydrated electron have been performed to unravel the structure of the hydrated electron.[3] Considering the ground state as a s-like state, the existence of quasi-degenerate p-like states in water is reported, calculations providing a separation between the p levels of approximately 0.5 eV.[4]

During the last 30 years, the reactivity of the hydrated electron has been widely studied, mainly by pulse radiolysis experiments. Therefore, a wealth of information on the reduction of metal ions in aqueous solution has also been obtained.[5] However, alkaline metal ions, such as Na^+, Li^+ and Cs^+, cannot be reduced in aqueous solution but they can form a pair with the solvated electron (M^+, e_s^-) in polar liquids. In that case, the optical absorption spectrum of the pair is blue shifted compared to that of the solvated electron.[6] Several studies in water have showed a shift of the absorption spectrum of the hydrated electron in the presence of metal ions. Anbar and Hart observed by electron pulse radiolysis measurements that the maximum of the hydrated electron shifts from 720 nm to shorter wavelengths in very concentrated aqueous solutions of KF (7.0 M), $NaClO_4$ (10 M), and LiCl (15 M).[7] Kreitus studied the optical characteristics of pulse radiolytically generated electrons in LiCl solutions over the concentration range 0−15 M.[8] More recently Krebs and co-workers resumed carefully the work on LiCl aqueous solutions and showed that the blue shift of the absorption band of the solvated electron with increasing the LiCl concentration is continuous without any change in the absorption band shape.[9] Lately, molecular dynamics simulations have reproduced the experimental UV−vis spectra and showed the

formation of a contact cation/electron pair in the case of sodium cation in water.[10] Those studies concern the hydrated electron paired with monovalent metal cations. Only a few data exist on the radiolysis of aqueous solutions containing alkaline earth metal cations.[11] In the earliest studies, from the measured yield of molecular hydrogen produced by γ-radiolysis of water in the presence of different metal cations it was concluded that Mg^{2+}, Ca^{2+} and Ba^{2+} do not react with the hydrated electron.[12] Recently that result was confirmed by observing that the decay of the hydrated electron is not affected by the presence of different concentrations of Mg^{2+}.[13] Indeed, as for alkaline metal cations, the reduction of hydrated Mg^{2+} by the hydrated electron does not occur because the value of the redox potential of the Mg^{2+}/Mg^+ couple is much lower than that of the hydrated electron. That is also true for the other alkaline earth metal cations, Ca^{2+}, Ba^{2+}, and Sr^{2+}. Concerning trivalent metal cations, only the lanthanide series presents stable free trivalent ions in aqueous solutions. In contrast to the first studies,[14] Gordon and co-workers found that Pr^{3+}, Nd^{3+}, Dy^{3+}, and Lu^{3+} are reduced very slowly (rate constants on the order of 10^6 mol^{-1} L s^{-1}) by the hydrated electron due to their electronic shell configuration and that the reaction rate constant between Tb^{3+} and the hydrated electron is even lower than 10^6 mol^{-1} L s^{-1}.[15]

Consequently, we choose Tb^{3+} and Mg^{2+} to study for the first time the influence of trivalent and divalent cations on the absorption spectrum of the hydrated electron. In the present paper, we show our primary results concerning the effects of salt concentration, cation charge, and counterion.

Experimental Section

We produced the hydrated electron mostly by two 263 nm photon ionization of water with femtosecond laser pulses but also by one-photon detachment from Cl^- in the case of chloride salts. The experimental pump−probe setup has already been detailed elsewhere.[16] Briefly, the laser system used for the present experiments was a regenerative amplified Ti:sapphire laser (Spectra Physics) that produced pulses at 790 nm with a duration of 110 fs and an energy of 1 mJ at a 1 kHz repetition rate. The pump beam at 263 nm was obtained by third harmonic generation with two BBO crystals while the probe beam was a white light continuum generated in a sapphire plate. After the sample was scanned, the probe beam was dispersed on a 300

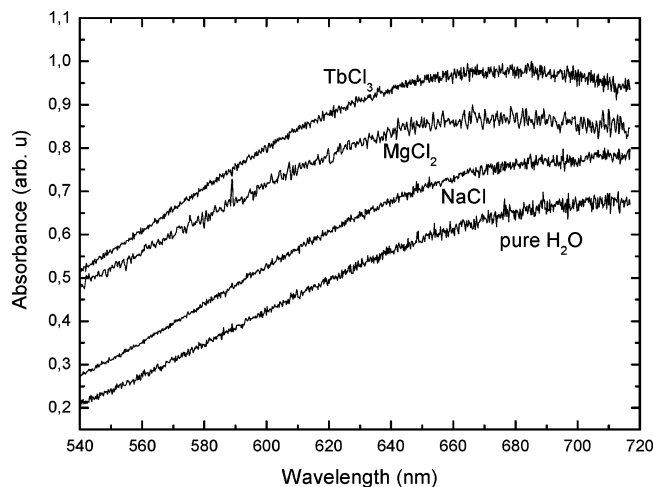* To whom correspondence should be addressed. E-mail: mehran.mostafavi@lcp.u-psud.fr.

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Figure 1. Optical absorption spectra of solvated electrons at 10 °C in pure water and in aqueous solutions containing 2 mol kg^{-1} of monovalent (Na), divalent (Mg), and trivalent (Tb) metal chloride salts.

Figure 2. Optical absorption spectra of solvated electrons at 10 °C in pure water and in aqueous solutions of magnesium perchlorate, Mg-$(ClO_4)_2$, with increasing concentration (1, 2, and 3 mol kg^{-1}).

mm polychromator (300 grooves/mm grating blazed at 500 nm) and detected on a 1340 × 400 CCD camera (Princeton Instruments), simultaneously with a reference beam to take into account any laser fluctuations. The detection setup is calibrated with the lines of a Ne lamp and controlled before each experiment with the well-known absorption band of the hydrated electron in pure water. In this manner, absorption spectra ranging from 450 to 725 nm were measured with a spectral resolution better than 1 nm. We used a sapphire nozzle to produce thin (300 μm) jets of the studied aqueous solutions which were cooled to 10 °C in order to improve the quality of the laminar flow. As the electron solvation dynamics is very fast in aqueous solutions and lasts less than a few picoseconds, the visible absorption spectrum of the equilibrated solvated electron for each solution was recorded 20 ps after the pump laser pulse. The observed absorption spectra are fitted with the Gaussian and Lorentzian shape functions at the low- and high-energy sides to find the maximum of the absorption spectra.[17]

The solutions were prepared using ultrapure water from a Millipore system (18.2 MΩ cm) and all the reagents were pure chemicals: NaCl (99,8%, Riedel-De Haën), MgCl$_2$,6H$_2$O (99% Aldrich), Mg(ClO$_4$)$_2$,6H$_2$O (99% Aldrich), TbCl$_3$,6H$_2$O (99,9% Alfa Aesar), and NH$_4$Cl (Prolabo).

Results and Discussion

Figure 1 presents the absorption spectrum of the solvated electron produced by irradiation with 263 nm photons in pure water and in three aqueous solutions containing 2 mol kg^{-1} of NaCl, MgCl$_2$, or TbCl$_3$ at 10 °C. In the presence of chloride salts, the yield of formation of the solvated electron is higher than that in neat water. Indeed, as an significant concentration of chloride anions is present in solution, the solvated electrons are produced by the one-photon photodetachment from charge-transfer-to-solvent (CTTS) of the Cl$^-$ anions in competition with the two-photon ionization of the solvent. In Figure 1, we observe that the maximum of the absorption spectrum is located at 710, 695, 685, and 670 nm for pure water and in the presence of NaCl, MgCl$_2$, and TbCl$_3$ respectively. It is to be noted that, at 10 °C, the absorption band maximum of the hydrated electron at 710 nm is slightly shifted toward shorter wavelengths compared to the maximum at 25 °C (720 nm), in agreement with previously reported results.[17] By adding chloride salts, we note that the absorption band maximum goes on shifting toward the shorter wavelengths while the shape of the absorption band
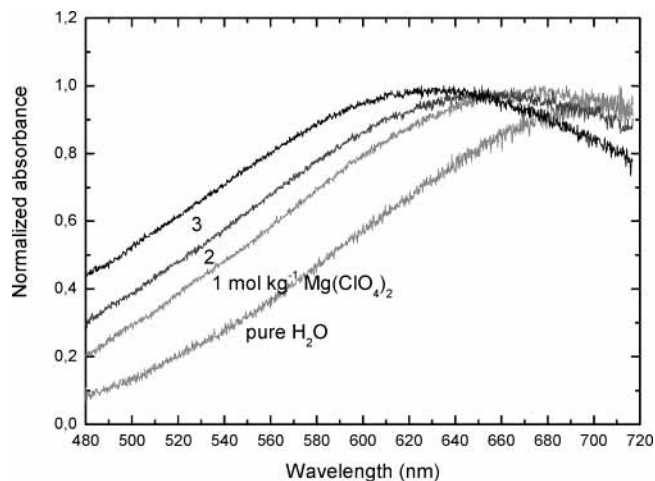
remains similar. For the same concentration of metal cation, the shift increases with the charge of the metal cation, indicating an electrostatic effect on the energy levels of the solvated electron.

The influence of the salt concentration on the solvated electron absorption spectrum is shown in Figure 2 which presents, as an example, the normalized absorption spectra recorded in aqueous solutions containing different concentrations of magnesium perchlorate. As the salt concentration increases, the spectrum shifts to shorter wavelengths. So, the absorption band maximum is around 665, 640, and 625 nm for 1, 2, and 3 mol kg^{-1} respectively. Such a shift of the hydrated electron absorption spectrum as a function of salt concentration was systematically investigated in the case of LiCl.[9] It is also worth noticing that the counterion plays a role on the spectral shift of the solvated electron spectrum since, for the same salt concentration (2 mol kg^{-1}), the absorption band maximum is situated at 650 nm for Mg(ClO$_4$)$_2$ and 685 nm for MgCl$_2$. The blue shift is higher in the case of perchlorate than chloride. As the perchlorate salt is more dissociated in water than the chloride one, the counterion effect may be related to the dissociation efficiency of the salts in water. Indeed, if the salt is not fully dissociated, the counterion in the vicinity of the metal screens the cation charge, which diminishes the interaction with the solvated electron.

In Figure 3, we compare the position of the electron absorption band maximum as a function of the salt concentration obtained for different chloride salts. We remark that, whatever the salt, the absorption band maximum moves toward the blue spectral domain as the concentration is increased. Moreover, the spectral shift is the more important as the charge of the cation is high. Nevertheless, the charge is not the only parameter involved since for the same charge Na$^+$ induces a larger shift than NH$_4^+$, and by comparing our results with those of ref 9, Li$^+$ seems to induce the largest shift.[9] That difference could be related to the size of the ion, the interaction with the electron decreases as the charge is less pointlike. Consequently, for each cation we simply calculate the surface and volume charge densities taking into account the charge and the ionic radius[18] (Table 1). That simple reasoning can explained the results of monocharged cations but fails completely in the case of Mg^{2+}. That highlights the complexity of the system and suggests that the influence of the counterion cannot be neglected. In particular, at high concentrations, the salts are not fully dissociated, and
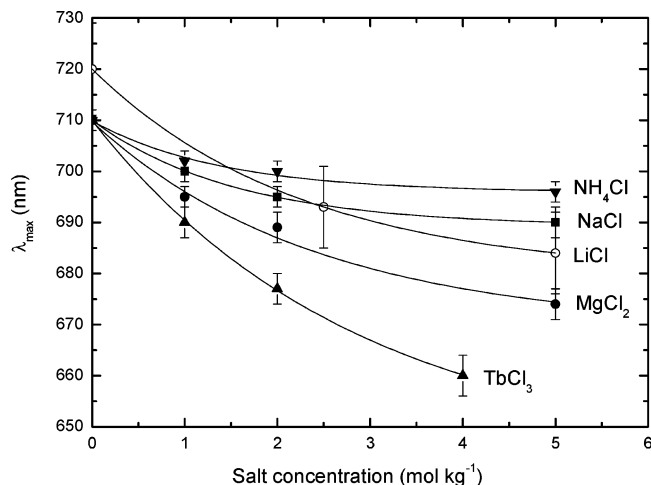
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Figure 3. Position of the maximum of the absorption band of the solvated electron, λ_{max}, as a function of the chloride salt concentration at 10 °C (ammonium, sodium, magnesium and terbium, respectively). The results concerning Li$^+$ (from Krebs et al.[9]) are performed at 25 °C.

TABLE 1: Ionic Radius (R) and Calculated Surface (σ) and Volume (ρ) Charge Densities of the Studied Cations

cation	R (pm)[18]	σ (C m^{-2})	ρ (10^{10} C m^{-3})
NH$_4^+$	143	0.62	1.31
Na$^+$	102	1.22	3.60
Li$^+$	76	2.20	8.70
Mg^{2+}	72	4.92	20.47
Tb^{3+}	118	2.74	6.97

for multicharged cations (Mg^{2+} and Tb^{3+}), several equilibriums exist in solution.

Conclusion

We have recorded the absorption spectra of the solvated electron in water in the presence of different salts at high concentration. A shift of the maximum of the absorption band toward shorter wavelengths is observed for the first time in the case of divalent (MgCl$_2$, Mg(ClO$_4$)$_2$) and trivalent (TbCl$_3$) metal salts. That shift increases with the salt concentration and the cation charge. Indeed, in the presence of high salt concentration, the electron is paired with the cation and its ground and excited states are affected. However, our results show that, for a given charge, the spectral shift depends on the nature of the cation

and also on the counterion. Further investigations (time-resolved solvation dynamics measurements and molecular dynamics simulations) are under way to complete this study and to bring a general explanation on the observed shifts in terms of cation charge, salt dissociation and properties of the aqueous salt solutions for the different cations.

References and Notes

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