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Absorption spectrum of the hydrated electron paired with nonreactive metal cations

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Abstract

We studied the effects of eight chloride and five perchlorate salts of monovalent, divalent or trivalent metal cations at high concentration in water on the optical absorption spectrum of the hydrated electron. Whatever the salt, the maximum of the hydrated electron absorption spectrum shifts toward shorter wavelength (''blue shift'') as the salt concentration is increased. The effects of the salt concentration, cation charge and counterion on the blue shift are discussed.

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1. Introduction

Observed for the first time in aqueous solutions of carbonate salts (Hart and Boag, 1962), the hydrated electron has been the subject of extensive works ever since. Its absorption spectrum was determined in this first study and appeared to be a broad, structureless band with a maximum around 700 nm in pure water. Because of the great interest of water in chemistry, biochemistry and physics, the hydrated electron is still an intense research subject to clarify its structure, both in experimental (Migus et al., 1987; Gauduel et al., 1990; Long et al., 1990; Alfano et al., 1993; Laenen and Roth, 2001) and theoretical aspects (Schnitker et al., 1988; Walqvist et al., 1988; Neria et al., 1991). Several simulations on the hydrated electron were performed (Schnitker and Rossky, 1987; Rossky and Schnitker,

1988; Motakabbir et al., 1989; Ludwig et al., 2004). The ground state is considered to be an *s*-like state, and the existence of quasi-degenerate *p*-like states is reported; theoretical calculations indicate an $\sim 0.5\,eV$ separation between the *p* levels (Bratos and Leicknam, 1996; Bratos et al., 1997; Nicolas et al., 2003).

The reactivity of the hydrated electron with different solutes, such as aliphatic, aromatic or heterocyclic compounds, and also anions and cations (Hart et al., 1964; Thomas et al., 1964; Baxendale et al., 1965) has been widely studied. During the last 35 years, a lot of information has been obtained on the reactivity of the hydrated electron, mainly by pulse radiolysis. The data about the reduction of metal ions were compiled in 1988 and 1995 (Buxton et al., 1988, 1995). Pulse radiolysis studies of aqueous solutions containing alkaline or earth alkaline metal ions showed that the hydrated electron does not react with these metal ions but forms ion pairs.

The first publication on the effect of unreactive metal cations on the absorption spectrum of the hydrated electron was published in 1965 (Anbar and Hart, 1965). These pulse radiolysis measurements in very concentrated

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aqueous solutions of KF (12.2 M), $MgCl_2$ (4.6 M), $NaClO_4$ (10 M) and LiCl (15 M) showed that the absorption maximum of the hydrated electron shifts from 720 nm in neat water to shorter wavelengths while the shape of the absorption band remains similar. The origin of that blue shift was attributed to a contraction of the radius of the electron cavity available to the ion in solution. Then, a few studies mentioned the observation of a blue shift of the absorption spectra in concentrated aqueous solutions of NaCl (Peled et al., 1972), LiCl, CsCl (Woods et al., 1975; Hankiewicz and Schulte-Frohlinde, 1977), in ethers and ammonia (Bockrath and Dorfman, 1973; Salmon et al., 1974; Fletcher and Seddon, 1975; Seddon et al., 1977), in alcohols (Hickel, 1978) or in frozen alkaline solutions (Kroh and Polevoi, 1978; Czerwik et al., 1986) without giving a global explanation of the phenomena, except reporting an electrostatic effect of the cation on the ground and/or first excited state of the hydrated electron due to the decrease of the electron cavity size.

The first systematic study of the salt concentration effect on the hydrated electron absorption spectrum was done by Kreitus (1985) in very concentrated (0–15 M) aqueous solutions of LiCl. He showed that increasing the salt concentration induces a nonuniform blue shift that can be explained by the formation of local microstructures, and that the absorption spectrum evolves differently in the low- and high-energy parts of the spectrum. In recent years, due to the development of an ultrafast laser pump–probe setup (Yokoyama et al., 1998), a few publications (Gelabert and Gauduel, 1996; Assel et al., 1998) noted a blue shift of the absorption band of the hydrated electron in the presence of a high concentration of NaCl and attributed it to a change in the hydration energy of the electron. In 1999, Krebs and co-workers (Asaad et al., 1999) resumed work on LiCl aqueous solutions and showed that the blue shift increased continuously with concentration without any change in the absorption band shape. To our knowledge, no other experimental result exists on the effect of metal salt concentration on the absorption band of the hydrated electron.

Recently, molecular dynamics simulations showed the possible formation of a contact cation–electron pair in the case of sodium cation. The simulation of the pair also showed a blue shift of about 0.3 eV from the hydrated electron spectrum attributed to a destabilization of the p-like state in the close presence of the cation (Spezia et al., 2004).

In this situation, we decided to start a general study on the influence of monovalent, divalent and even trivalent nonreactive metal cations on the absorption spectrum of the hydrated electron. Indeed, in the same way as for the alkaline metal cations, alkaline earth metal cations are not reduced by the hydrated electron as the redox potential of the M^{2+}/M^{+} couple is lower

than the redox potential of the hydrated electron. But up to now, for divalent metal cation, only the effect of Mg^{2+} was studied at the beginning of the discovery of solvated electrons (Anbar and Hart, 1965). Regarding trivalent metal cations, only the lanthanide series presents stable free ions in aqueous solutions. These ions are reduced very slowly by the hydrated electron. Tb^{3+} presents a reaction rate constant with the hydrated electron even lower than $10^6\,mol^{-1}\,L\,s^{-1}$ (Gordon et al., 1977). Therefore, it is possible to observe the pair formation between Tb^{3+} and hydrated electrons. Preliminary results on Mg^{2+} and Tb^{3+} have already been published (Bonin et al., 2004). In the present paper, we show our global results concerning the effects of charge, salt concentration and counterion.

2. Experimental

The hydrated electrons were mostly produced by two 263 nm photon ionization of water molecules (Eq. (1)) with femtosecond laser pulses but also by one-photon detachment from Cl^- (Eq. (2)) in the case of chloride salts:

$$H_2O \xrightarrow{2h\upsilon} H_2O^+ + e^- \longrightarrow e^-_{hyd} \tag{1}$$

$$Cl^- \xrightarrow{h\upsilon} Cl^\bullet + e^-_{hyd} \tag{2}$$
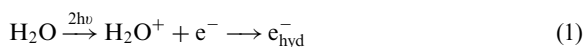
The formation of a chloride radical induces a dismutation with the chloride anion to form Cl_2^- (Eq. (3)), a species absorbing at 340 nm (Grossweiner and Matheson, 1957; Anbar and Thomas, 1964).

$$Cl^\bullet + Cl^- \longrightarrow Cl_2^- \tag{3}$$

Thus, the measured spectra we present here cover the visible domain from 480 nm to exclude any additional absorption from Cl_2^-.

The experimental pump–probe setup (Fig. 1) has already been detailed elsewhere (Soroushian et al., 2004). Briefly, the laser system is a regenerative amplified Ti:sapphire laser (Spectra Physics) that produces pulses centered 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 264 nm is obtained by third harmonic generation (THG) with two BBO crystals and the probe beam is a white light continuum generated in a sapphire plate. Once the sample is scanned, the probe beam is dispersed on a 300 mm polychromator (300 groves/mm grating blazed at 500 nm) and then detected on a 1340×400 CCD camera (Princeton Instruments) simultaneously with a reference beam that allows one to take into account any laser fluctuations. The detection setup is calibrated with the Ne lamp lines and controlled previously to each experiment with the well-known absorption spectrum of the hydrated electron in pure water. In this configuration, absorption spectra were
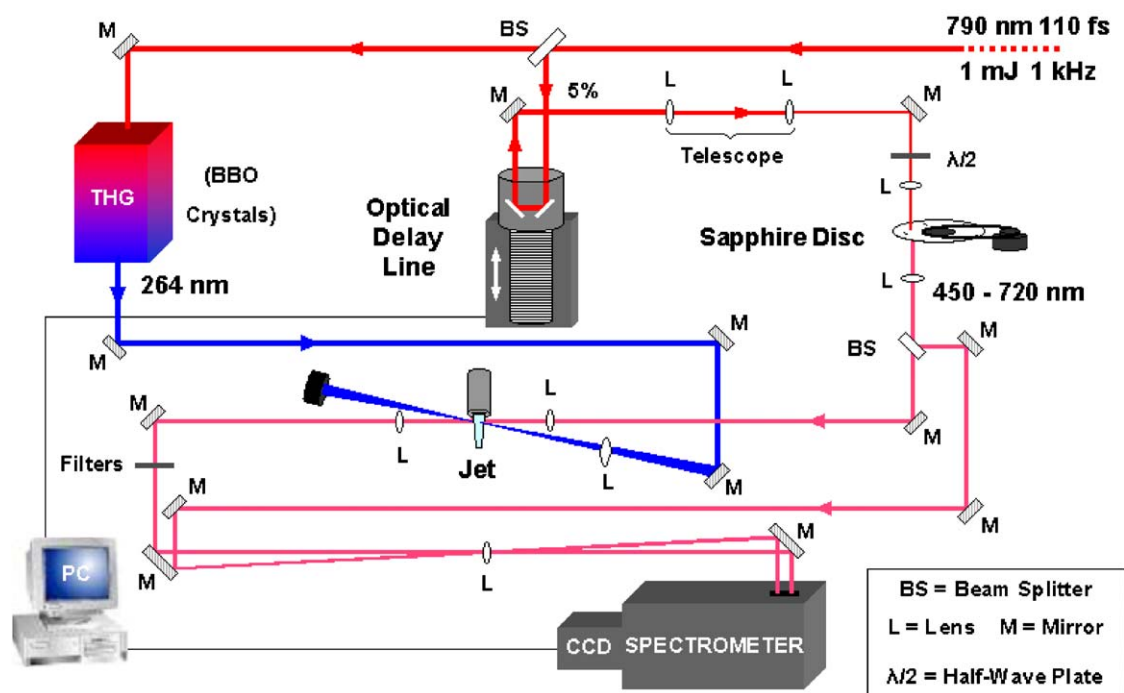
Fig. 1. Scheme of the experimental laser pump–probe setup.

recorded between 480 and 720 nm with a spectral resolution less than 1 nm. Thin jets (300 μm) of the studied solutions were produced by a sapphire nozzle and samples were cooled at 10 °C to improve the quality of the laminar flow jet. The electron solvation dynamics in aqueous solutions is very fast and lasts a few picoseconds so the visible absorption spectrum of the equilibrated hydrated electron 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 determine the position of the maximum (Jou and Freeman, 1979).

The solutions were prepared using ultrapure water from a Millipore system (18.2 MΩ cm) and all the salts were pure chemicals: LiCl (99%, Merck), NaCl (99.8%, Riedel-deHaën), CsCl (99%, Aldrich), NH_4Cl (pure, Prolabo), $MgCl_2 \cdot 6H_2O$ (99%, Aldrich), $CaCl_2 \cdot 2H_2O$ (99.5%, Fluka), $SrCl_2$ (99%, Aldrich), $TbCl_3 \cdot 6H_2O$ (99.9%, Alfa Aesar); the perchlorate salts come from Aldrich: $LiClO_4 \cdot 3H_2O$, $NaClO_4 \cdot xH_2O$ (99%), $Mg(ClO_4)_2 \cdot 6H_2O$ (99%), $Ca(ClO_4)_2 \cdot 4H_2O$ (99%) and $Sr(ClO_4)_2 \cdot xH_2O$.

3. Results and discussion

Fig. 2 presents, as an example, the influence of the CsCl salt concentration on the absorption spectrum of the hydrated electron. In this figure, the absorption spectra of the hydrated electron produced by irradiation with 263 nm photons in pure water and in aqueous solutions with increasing concentration (1, 2, 5 and 7 mol kg^{-1}) of CsCl at 10 °C are shown. First, the increasing absorbance with concentration is due to the higher yield of hydrated electrons formation in the presence of chloride salt than in neat water because of the very efficient one-photon detachment from Cl$^-$ (reaction (2)). Indeed, as a substantial concentration of chloride anions is present in solution, there is a competition for the production of hydrated electrons between the direct two-photon ionization (reaction (1)) of solvent molecules and the one-photon detachment from charge transfer to solvent (CTTS) of the Cl$^-$ anions. Second, we observe that the maximum of the absorption spectrum is peaked around 710, 700, 695, 685 and 680 nm for pure water and for 1, 2, 5 and 7 mol kg^{-1} of CsCl, respectively. In agreement with previous publications (Gottschall and Hart, 1967; Michael et al., 1971; Jou and Freeman, 1979), we notice that the absorption band maximum of the hydrated electron at 10 °C is slightly shifted (710 nm) toward shorter wavelengths compared to 25 °C (720 nm).

Fig. 3 presents the absorption spectrum of the hydrated electron in three aqueous solutions containing 5 mol kg^{-1} of CsCl and $CaCl_2$ and 4 mol kg^{-1} of $TbCl_3$ (the latter is not soluble at 5 mol kg^{-1}) at 10 °C. The blue
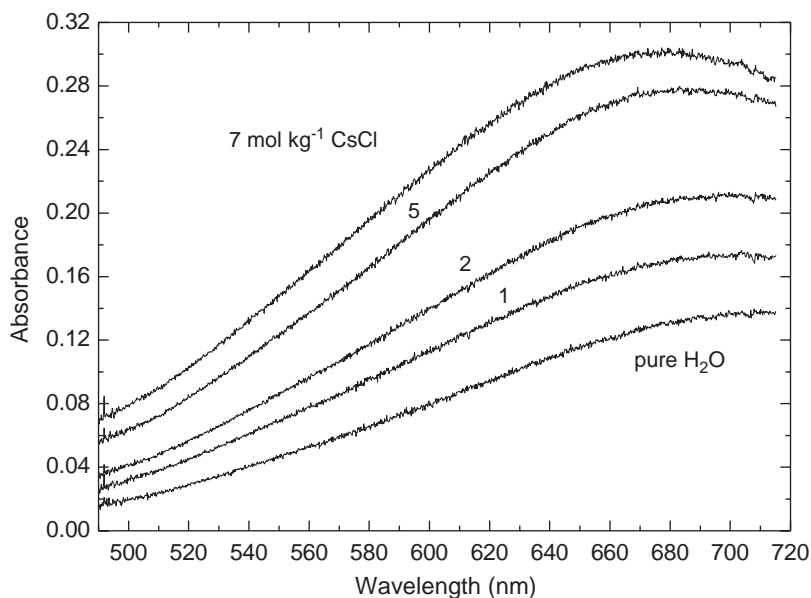
Fig. 2. Optical absorption spectra of hydrated electrons at $10\,^{\circ}C$ in pure water and in aqueous solutions of cesium chloride, with increasing concentration (1, 2, 5 and $7\,mol\,kg^{-1}$).

shift is more pronounced for $TbCl_3$ than for $CaCl_2$ and CsCl: the maximum of the absorption band is located at 685, 680 and 660 in the presence of CsCl, $CaCl_2$ and $TbCl_3$, respectively. As for CsCl solutions, the addition of chloride salts induces a shift toward shorter wavelengths and, for the same order of magnitude of concentration of metal cation, the shift increases with the charge of the cation, clearly indicating an electrostatic effect on the energy levels of the hydrated electron. Another information from our results is the shape stability of the hydrated electron absorption band, which is still a debate subject (Kreitus, 1985; Marbach et al., 1999). This is illustrated in Fig. 4: the absorption spectra of aqueous solutions of $TbCl_3$ (inset) were shifted in energy and normalized in intensity to obtain the energy profiles. It is clear that these profiles can be superimposed, that means the observed species is the hydrated electron all along the concentration range and that the shape of the absorption spectrum is not affected by the presence of the metal cation.

Table 1 gathers all the results of the position of the absorption band maximum as a function of the salt concentration for all the salts studied (eight chloride and five perchlorate salts). The maximum of the absorption band, E_{max}, as a function of the chloride salt concentration is presented in Fig. 5 for monovalent cations and in Fig. 6 for divalent and trivalent cations. First, we note that whatever the salt, E_{max} moves toward high energy (blue part of the spectral domain) as the concentration is increased. Second, the higher the cation charge, the more important the blue shift. This has also been
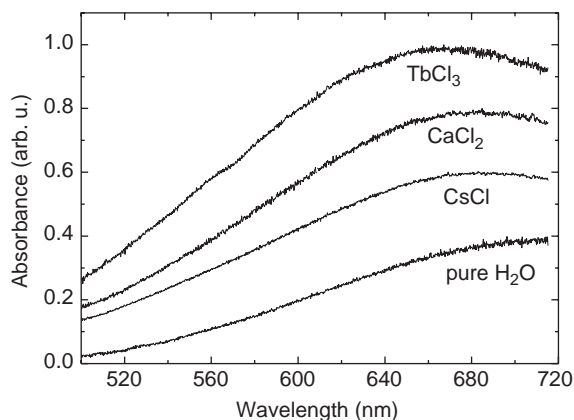

Fig. 3. Optical absorption spectra of hydrated electrons at $10\,^{\circ}C$ in pure water and in aqueous solutions containing $5\,mol\,kg^{-1}$ of monovalent (Cs) and divalent (Ca) and $4\,mol\,kg^{-1}$ of trivalent (Tb) metal chloride salts.

observed in aqueous solutions of perchlorate salts, as can be seen in Fig. 7, where the spectral shift is more important for the divalent cation (Ca^{2+}) than for the monovalent one (Na^+).

However, the charge is not the only parameter to take into account for the spectral shift, since, as it is clearly observable in Figs. 5 and 6, for the same charge, Li^+ induces a larger shift than Cs^+ and Mg^{2+} induces a larger shift than Sr^{2+}. Moreover, we notice that the counterion also plays an important role in the blue shift
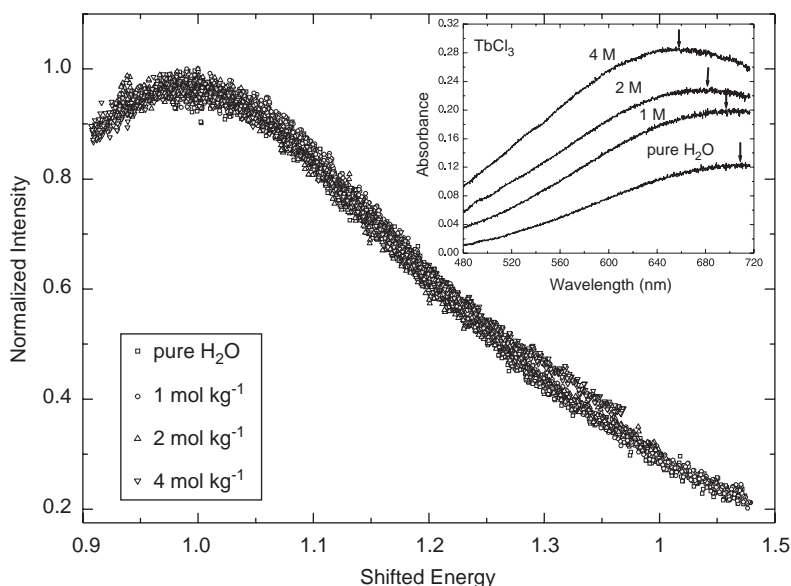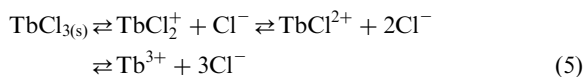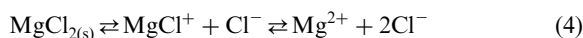
Fig. 4. Absorption spectra in aqueous solutions of TbCl$_3$ shifted in energy and normalized in intensity (called energy profiles, see text for more explanations).

since, for the same range of concentration, the absorption band maximum peaks at higher energy for Ca(ClO$_4$)$_2$ than CaCl$_2$ (Fig. 8). So, the blue shift is greater in the case of perchlorate than chloride. Given that the dissociation of the perchlorate salts in water is better than that of the chlorides, the counterion effect may be linked to the dissociation efficiency of the salts in water. Actually, in the case of an incomplete dissociation of the salt, as it surely happens in very concentrated solutions, the counterion in the vicinity of the metal screens partially the cation charge, and reduces the interaction with the hydrated electron.

The difference between cations with the same charge could be related to the properties of the ion, in particular their sizes. Indeed, the more pointlike the charge, the stronger the interaction with the hydrated electron. As a consequence, we calculate, for each cation, the surface (σ) and volume (ρ) charge densities (Table 2), considering the charge and the ionic radius (Lide, 1995). That simple reasoning can explain the results obtained for monocharged cations (Fig. 5). The most important blue shift is observed for Li$^+$, which has the greatest charge density by far, while the lowest blue shift is for NH$_4^+$, which has low charge densities and a high screening effect. The intermediate positions of Na$^+$ and Cs$^+$ are not separated enough, considering error bars, to conclude about the accuracy of the reasoning. In addition, the whole reasoning fails completely with Mg^{2+}, which has the largest charge densities of all the studied cations but does not induce the largest spectral shift (Li$^+$ and Tb^{3+}, with lower charge densities, induce

larger shifts). These assessments show the complexity of the solutions, and in particular that the role of the counterion must not be neglected. Indeed, at high concentrations, the salts are not fully dissociated, and, especially for the multicharged cations, several equilibria may exist in solution, as shown, for example, in Eqs. (4) and (5):

$$MgCl_{2(s)} \rightleftarrows MgCl^+ + Cl^- \rightleftarrows Mg^{2+} + 2Cl^- \tag{4}$$

$$TbCl_{3(s)} \rightleftarrows TbCl_2^+ + Cl^- \rightleftarrows TbCl^{2+} + 2Cl^- \\ \rightleftarrows Tb^{3+} + 3Cl^- \tag{5}$$

So, the main effect that induces the blue shift is a charge effect that depends on the nature of the cation, but in an important way on the solution characteristics, especially the salt dissociation: as a function of counterion, the cation is more or less free in solution, its charge being therefore more or less screened.

4. Conclusion

We performed a study on the effect of the presence of a nonreactive metal cation upon the hydrated electron by measuring its visible absorption spectra in concentrated aqueous solutions of eight chloride and five perchlorate salts, with monovalent, divalent and trivalent cations. We observed a shift of the absorption band maximum toward shorter wavelengths that increases with the salt concentration but also with the

Table 1
Wavelength and energy of the hydrated electron absorption band maximum as a function of salt concentration for all the studied salts and some previous works

C (mol kg⁻¹) λ_{max} (nm) ±3 nm / E_{max} (eV)	LiCl (a)	LiCl (b)	NaCl (a)	CsCl (a)	NH$_4$Cl (a)	MgCl$_2$ (a)	MgCl$_2$ (c)	CaCl$_2$ (a)	SrCl$_2$ (a)	TbCl$_3$ (a)	LiClO$_4$ (a)	NaClO$_4$ (a)	NaClO$_4$ (c)	Mg(ClO$_4$)$_2$ (a)	Ca(ClO$_4$)$_2$ (a)	Sr(ClO$_4$)$_2$ (a)
1	695 / 1.786	710 / 1.749	700 / 1.773	700 / 1.773	705 / 1.760	695 / 1.786		700 / 1.773	700 / 1.773	690 / 1.798	685 / 1.812	680 / 1.825		670 / 1.852	680 / 1.825	680 / 1.825
2	685 / 1.812	700 / 1.777	695 / 1.786	695 / 1.786	700 / 1.773	690 / 1.798		690 / 1.798	690 / 1.798	675 / 1.838	670 / 1.852	660 / 1.880		640 / 1.939	670 / 1.852	670 / 1.852
3									685 / 1.812					625 / 1.986		
4							4.6 M			660 / 1.880	645 / 1.924					
5	670 / 1.852	675 / 1.837	690 / 1.798	685 / 1.812	695 / 1.786	675 / 1.838	650 / 1.909	680 / 1.825				650 / 1.909			640 / 1.939	650 / 1.909
6								675 / 1.838								
7				680 / 1.825												
8												645 / 1.924				
10	660 / 1.880	635 / 1.952										605 / 2.052				

(a): this work ($T = 283$ K); (b): extrapolated from Asaad et al. (1999) ($T = 298$ K); (c): Anbar and Hart (1965) (room temperature).
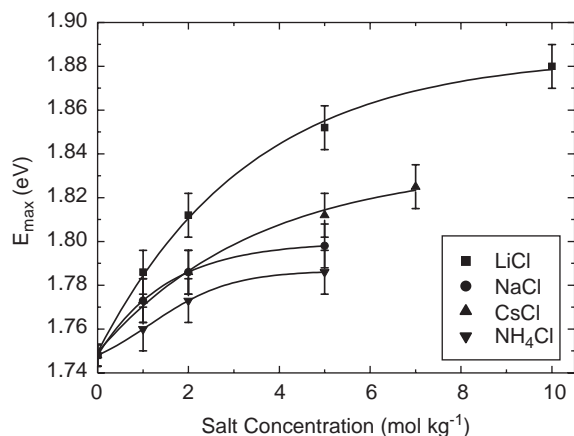
Fig. 5. Position of the maximum of the absorption band of the hydrated electron, E_{max}, as a function of the monovalent chloride salt concentration at $10\,°C$.
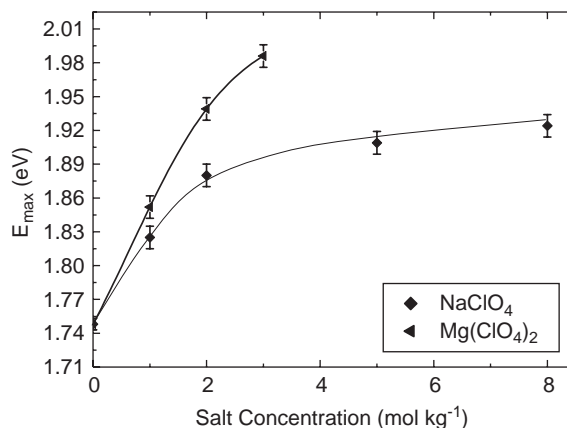

Fig. 7. Position of the maximum of the absorption band of the hydrated electron, E_{max}, in aqueous solutions of sodium and magnesium perchlorate as a function of concentration at $10\,°C$.
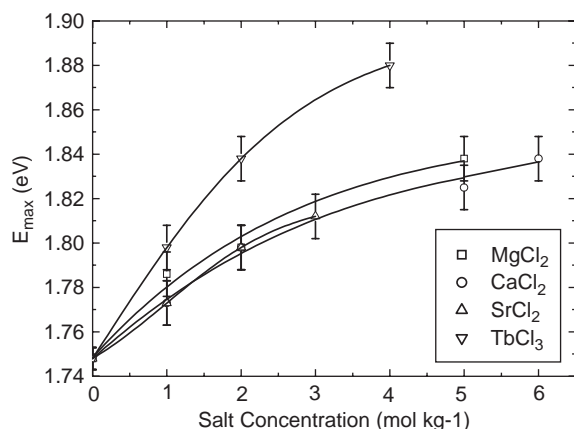

Fig. 6. Position of the maximum of the absorption band of the hydrated electron, E_{max}, as a function of the di- and trivalent chloride salt concentration at $10\,°C$.
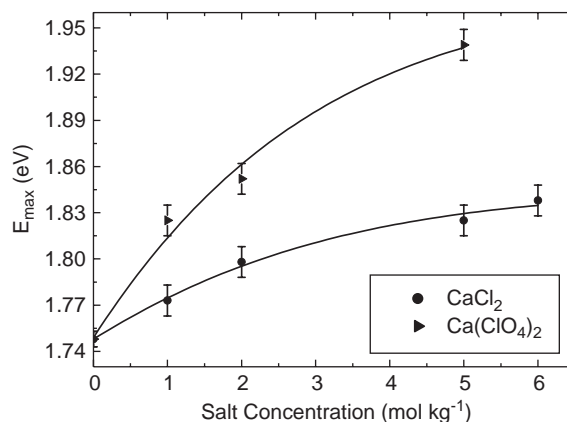

Fig. 8. Position of the maximum of the absorption band of the hydrated electron, E_{max}, for the calcium cation in chloride and perchlorate salts as a function of concentration at $10\,°C$.

cation charge. At high salt concentration, the hydrated electron forms an ion pair with the cation that affects its ground and excited states. The spectral shift depends on the characteristics of the solution such as cation size (through charge densities) or dissociation degree of the salt (partial screening of the cation charge when incomplete dissociation). The present study is also of fundamental interest when kinetics measurements are performed at high concentration, for example at very high pH (corresponding to a high concentration of Na^+ or K^+): the hydrated electron in such conditions is not free but associated (ion pair) in solution.

Table 2
Ionic radii (R), calculated surface (σ) and volume (ρ) charge densities of the studied cations

Cation	R (pm)	σ ($C\,m^{-2}$)	ρ ($10^{10}\,C\,m^{-3}$)
NH_4^+	143	0.62	1.31
Li^+	76	2.20	8.71
Na^+	102	1.22	3.60
Cs^+	174	0.42	0.72
Mg^{2+}	72	4.92	20.49
Ca^{2+}	100	2.55	7.65
Sr^{2+}	126	1.61	3.82
Tb^{3+}	118	2.74	6.98

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