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Solvation dynamics of electron–metal cation contact pairs in LiCl aqueous solutions†

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In this study, the dynamics of the solvation of (Li^+–electron) pairs were investigated in LiCl water solutions at concentrations ranging from 2 to 14.6 M. The dynamics of contact pair solvation were observed experimentally for the first time using picosecond electron radiolysis. We observed a clear concentration-dependent increase in electron solvation time – from 10.6 ps at a LiCl concentration of 3.5 M to 17.3 ps at 14.6 M. We provide a mechanistic description of how metal cations influence this solvation.

Introduction

Upon the introduction of an excess electron into liquid water, the resulting solvated entity is recognized as a hydrated electron (or solvated in the general case), e^-_{hyd}. Despite its significance, particularly in radiation chemistry, a comprehensive framework that accounts for all its physicochemical properties remains elusive.[1]

Following the discovery of the solvated electron, e^-_{hyd}, the impact of dissolved inorganic salts on the optical absorption spectrum of solvated electrons was investigated.[2] It was observed that an increase in salt concentration led to a shift in the maximum of the e^-_{hyd} absorption spectrum towards higher energies.[2] Seeking more insights, Kreitus[3] conducted a detailed examination of the solvated electrons in aqueous LiCl solutions, leveraging the high solubility and inertness of this salt. The optical absorptions of e^-_{hyd} produced radiolytically in LiCl solutions in H_2O and D_2O at 294 K were measured over a concentration range of 0–15 M. Kreitus reported abrupt spectral changes in hydrated electron absorption near certain stoichiometric compositions of LiCl. As the experimental results of Kreitus have very far-reaching consequences, it was necessary to repeat such measurements once more carefully, as done by Asaad *et al.*[4] In their work, they found that the spectral shift proceeds smoothly throughout the concentration range, which was in contrast to what was claimed by Kreitus.

Subsequently, Mostafavi *et al.*,[5] through laser photolysis, investigated the effects of chloride and perchlorate salts with non-reactive monovalent, divalent, or trivalent metal cations in water on the optical absorption spectrum of e^-_{hyd}. The blue spectral shift was dependent on the solution characteristics, such as cation size or the degree of dissociation of the salt (incomplete dissociation leading to partial screening of the cation charge).

Recently, Schwartz *et al.* revisited the topic of solvated electrons,[1,6–8] exploring the roles of cations and anions using mixed quantum/classical and molecular dynamics simulations, trying to understand the origin of the concentration-dependent spectral shift. They showed that the stability of the electron–cation contact pair arises from a delicate balance involving electron solvation, cation solvation, and cation–electron interactions. Minor alterations in any of these interactions can disrupt this balance, thus influencing the nature of electron–cation contact pairs.[1] Creating aqueous contact pairs (Me^+, e^-) results in the desolvation of sodium cations and electrons. It becomes apparent that a more favorable strategy under high electrolyte concentrations involves establishing multiple weak cation–electron interactions while preserving distinct water–electron and water–cation interactions rather than intensifying a single cation–electron interaction, even with the screening it provides.[7] Despite interest in this subject, in radiation-exposed biological environments, where electrons often form transient pairs with metal cations, the dynamics of pair formation and solvation remain poorly understood. In batteries, the electron–metal contact pairs could be of importance at high electrolyte concentrations, in the electronic processes at the electrodes. To the best of our knowledge, no experimental attempts were made to unravel the question of cation–excess electron interactions on short-time scales down to picosecond regimes in aqueous solutions. One can assume that the formed excess electrons would immediately sense the potential of cations and anions in the solution. However, our recent work, where a high concentration of sodium azide in water was used,[9] led to the

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conclusion that the overall solvation of metal cation–electron pairs occurs on much longer time scales up to several tens of picoseconds.[8] In the study, it is affirmed that an excess electron in water tends to localize directly at the sites of Na^+ traps. This observation aligns closely with our findings, where a significant blue shift in the hydrated electron absorption band was already evident within a 5 ps electron pulse. However, the gradual continuation of the absorption band shift takes an overall 50 ps to complete. Consequently, our investigation on azide reactivity with presolvated electrons marks a new experimental phase in the exploration of interactions between hydrated electrons and metal cations.[9]

An electron–metal cation pair formation is known not only for water but also for other solvents. As observed in THF solution, non-dissociated magnesium perchlorate salt could be bound to solvated electrons, forming reducing species capable of reducing different aromatic molecules in solution.[10,11]

In this work, we employed 5 ps electron pulse radiolysis to investigate how varying LiCl concentrations influence the solvation dynamics of cation–electron pairs. We chose LiCl due to its notably high solubility in water, enabling concentrations approaching 15 M.

Experimental

The pulse radiolysis experiments were conducted using the ELYSE platform at the University of Paris-Saclay. This platform couples an electron accelerator providing 5 ps pulses (5 Hz, 7 MeV, 6 nC) with a transient absorption spectroscopy system covering the range of 350–800 nm. The measurements were conducted in static 5 mm quartz cells. Additional details can be found elsewhere.[12]

Metal chloride salts were procured from Sigma-Aldrich and used without further purification.

A highly concentrated LiCl stock solution was prepared in a 10 mL volumetric flask as follows. First, approximately half of the required salt mass (plus a 5% surplus) was added to the flask, and water was then added to bring the total volume close to 10 mL. The mixture was heated and stirred until the initial portion of the salt dissolved. Next, the remaining salt was gradually introduced under vigorous stirring at near-boiling temperatures. Afterward, the solution was cooled (the solution level could exceed 10 mL), a white haze appeared, a small portion of the solution was removed and replaced with fresh water to reach a 10 mL volume, followed by reheating until the solution became transparent. This heat–cool–dilute cycle was repeated until no haze formed at room temperature. The final solution was left undisturbed overnight, allowing any further crystallization to proceed. Finally, a 14.6 M LiCl stock solution was obtained, which was verified by evaporating 1 mL of the solution and subsequently heating the residue at 300 °C overnight. All experiments were carried out at 22 °C.

Results and discussion

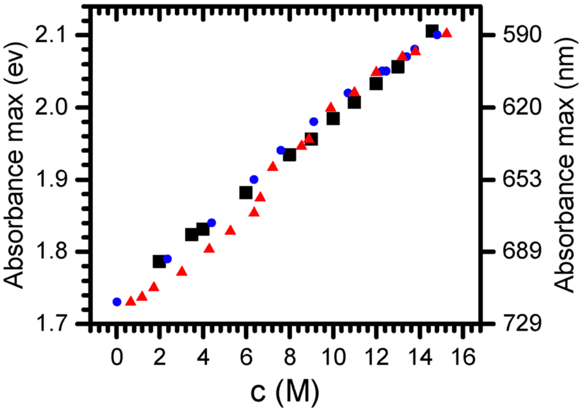

Fig. 1 The position of the e^-_{hyd} absorption maximum in LiCl water solutions at 22 °C at different concentrations (black squares) at 150–200 ps after the electron pulse; blue circles indicate the work of Asaad *et al.*;[13] red triangles indicate the work of Kreitus.[3]

Fig. 1 shows the e^-_{hyd} absorption-band maximum as a function of LiCl concentration (150–200 ps after solvation). The transient absorption maps for the measurements are readily available in the ESI† (the raw data can also be downloaded). The blue shift of the absorption maximum increases monotonically with LiCl concentration. We determined the absorption maximum by fitting a 60-nm window around the peak with a Gaussian function (after converting wavelength to energy).

At the earliest delays (during the electron pulse), the absorption maximum is already blue-shifted for all LiCl concentrations. The higher the salt concentration, the more pronounced this initial blue shift, and the higher the charge (see the ESI† for Mg^{2+}, Na^+ and Tb^{3+} data) of the metal cation, the more pronounced this shift with respect to concentration (see Fig. 3). Our LiCl data align well with those reported by Asaad *et al.*[13] The peak position of e^-_{hyd} changes monotonically, without the abrupt changes reported by Kreitus.[3]

The initial blue shift observed just after the electron pulse is related to the fact that the excess electron finds its metal cation trap within the ionization pulse (<5 ps). As time goes on, the absorption band maximum continues to shift. The time constants for the solvation of metal cation–electron pairs are presented in Fig. 4. The spectral shift was fitted with an exponential function (Fig. 3) for each concentration. The time when the spectral shift stabilizes depends on the concentration of the solution directly: the higher the concentration, the slower the process and the bigger the shift. In such a way, we can state that the metal cation initially traps the excess electron; it undergoes its solvation, forming a (Me^+, e^-) pair. Such a pair further continues its solvation much more slowly than the initial excess electron solvation that occurs on a subpicosecond time scale.

Bonin *et al.*[5] previously conducted a similar study; the observed changes in most cases are similar to our data. However, they did not analyze the dynamics; instead, they fixed the delay between the ionization pulse and detection at 20 ps. Consequently, the findings presented by Bonin *et al.* reflect an electron absorption shift that is only partially complete.

It is worth mentioning that the shape of the absorption band is slightly altered. Overall, we observe not only a spectral shift but also a slight broadening of the absorption band (Fig. 2). We

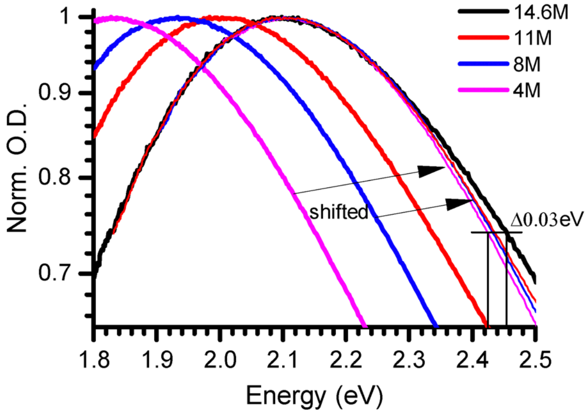

Fig. 2 The spectra of e^-_{hyd} for different salt concentrations at 150–200 ps after the electron pulse. Curves for 11 M, 8 M and 4 M were shifted to overlay with the 14.6 M curve.

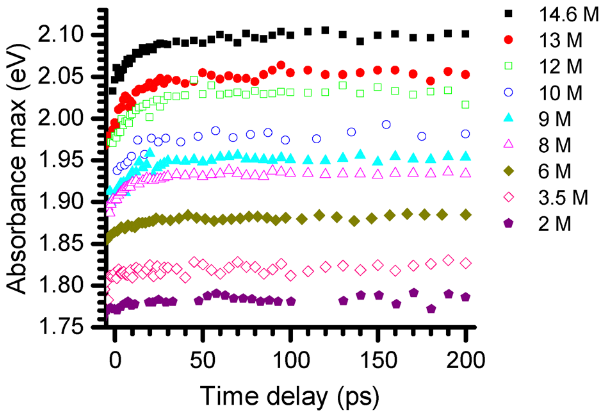

Fig. 3 Time dependence dynamics of the e^-_{hyd} absorption maximum in LiCl water solutions at 22 °C at different concentrations.

observed the full width at half maximum of the absorption band to change by just 0.03 eV between 4 M and 14.6 M, within our experimental uncertainty. A detailed theoretical model would be required to rationalize such a subtle variation, which is outside the scope of this study. This difference (Fig. 2) is similar to what was presented by Asaad *et al.*,[13] who reported the width at half-height for pure water to be 0.84 eV and 0.87 eV for the highest concentration of LiCl they investigated.

The process of solvation slows down with increasing concentration. This phenomenon can be understood by considering that water concentration is around 55 M. In situations where there is a high salt concentration, such as 14.6 M LiCl, all water molecules are engaged in forming solvation shells around both cations and anions.‡ At high salt concentrations, we do not have fully dissociated salt molecules, but rather water clusters surrounded by partly and non-dissociated salt molecules.§ The solvation time constants are summarized in Fig. 4. Explaining the linear concentration–lifetime trend by viscosity alone is misguided, since LiCl solution viscosity is strongly non-linear with concentration.[15]

Li^+, with its high polarizing power, strongly orders nearby water molecules by reducing their mobility, forming a tightly bound tetrahedral first hydration shell. In contrast, Cl^- slightly disrupts water's hydrogen-bond network by forming weaker bonds with approximately six water molecules along the OH directions. Overall, Li^+'s structure-making effect predominates in LiCl solutions, leading to reduced translational and rotational movements of water compared to pure water. Van Wyc *et al.* revealed that, at low ion concentrations, the water behaves much like pure water. Still, as more LiCl is added, the formation of large, more slowly relaxing ion–water networks becomes dominant. This change not only alters the microscopic dynamics but also explains the macroscopic increase in viscosity observed in these concentrated solutions.[16]

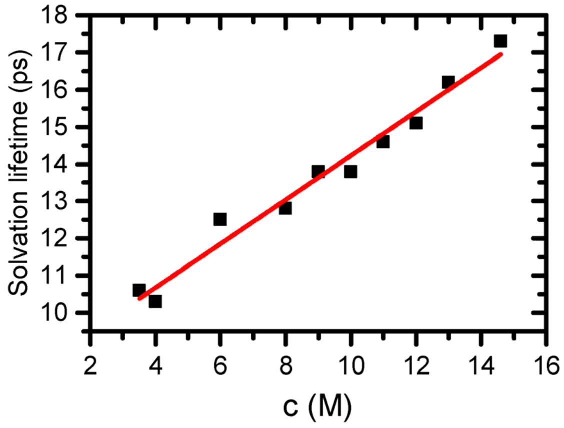

Fig. 4 Solvation lifetime dependence on LiCl concentration.

As observed previously by Bonin *et al.*,[17] the strength of spectral shift depends not only on the concentration and nature of the salt but also on the counter-ion as well. We expect to have different solvation dynamics for salts of different chemical origins due to higher or lower degrees of dissociation, microviscosity, and solvation shell energetic characteristics.

Drawing from our experimental findings and basic knowledge of the solvation dynamics of electrons in liquids, we suggest a mechanistic representation of electron solvation at high metal cation concentrations. At lower concentrations, electron solvation involves mainly free water molecules, yet metal cations influence this process, leading to a small and rapid solvation shift. At higher concentrations, electrons still engage some free water, but much of their solvation shell derives from cation-bound water. Solvation then proceeds more slowly, since the presolvated electron must reorganize the cation's tightly bound hydration shell. The more pronounced blue shift reflects stronger electron stabilization by nearby metal cations. At very high salt loadings, when almost all water is tied up in ionic hydration shells, electron solvation proceeds by reorganizing water within the cation's shell, encountering a higher activation barrier (Fig. 4). The pronounced blue shift can

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‡ At such a concentration, the ratio of H_2O : LiCl molecules is 2.6.

§ The activity of LiCl solution decreases from 0.996 at a low concentration to 0.11 at the highest concentration.[14]

be attributed to interactions between an electron and two or more cations simultaneously, made possible as the average distance between cations reduces to 0.7 nm already at 4.5 M, roughly the span of three water molecules, facilitating this dual cation interaction. For simplicity, we do not consider here the effects of anions' nature or viscosity changes at high salt concentrations, as well as the effects of the presence of non-dissociated salt molecules, which is not negligible for understanding solvation dynamics.

Chemists traditionally plot solvation parameters against molarity (M), but this can obscure the true physical scaling. In a simple, non-aggregating, fully dissociated solution, the average intermolecular spacing d varies as $d \approx (0.602 \times c)^{-1/3}$. Hence, a property that depends nonlinearly on the average distance can nonetheless appear linear when plotted against M. Both the hydrated-electron absorption maximum and the solvation time therefore exhibit an almost linear trend *versus* concentration—even though their dependence on the underlying intermolecular distance is intrinsically nonlinear.

Certainly, the charge density of metal cations significantly influences the spectral shift observed in solvated electrons. Notably, the smaller Li^+ ion exhibits a more pronounced shift (*ca.* 677 nm) compared to Na^+ (*ca.* 680 nm) at identical concentrations. In contrast, the blue shift with Mg^{2+} extends to approximately 630 nm (see the ESI†). This observation aligns with the positions of cations on the Hofmeister series, where Li^+ is more chaotropic (*i.e.*, water-disrupting) than Na^+, but less than Mg^{2+}. It should be noted that, at high concentrations, $MgCl_2$ does not fully dissociate but remains in the form of $MgCl^+$.

Narvaez *et al.*[6] primarily focused on the influence of anions and also presented the effect of cations such as Na^+ and Ca^{2+}, confirming our observations. The trends observed with Tb^{3+} further support these findings, where the higher charge density leads to a notable blue shift (approximately 675 nm), even at a moderate concentration of 1.5 M (see the ESI†).

An important question that arises with respect to solvation dynamics is the temperature effect.[18] Increasing temperature induces a red shift, counteracting the salt-induced blue shift. How this competition affects electron-solvation dynamics in the presence of non-reactive cations remains unclear.

We aim to extend the gained insights to understanding electron behavior in biological contexts, such as cells. The process of electron solvation and the behavior of other radiation-induced radicals within cells, where the absence of free water due to high concentrations of organic and inorganic substances must have a significant impact, are of particular interest. There have been studies indicating that, in environments where space is limited, the dynamics of electron solvation are impeded, resulting in a prolonged lifespan of the presolvated electron, thereby enhancing its capture by nucleotides. Additionally, viscous solvents have been shown to decelerate electron solvation significantly. However, to our knowledge, this is the first study to demonstrate a direct modification of solvation dynamics in water, which is arguably the most vital solvent on the Earth.

Conclusions

In our work, we experimentally showed that, at high concentrations of metal cations, herein Li^+, the solvation of excess electrons in water is not only limited to the solvation of electrons at preexisting metal cation traps, but also leads to the formation of a metal cation–solvated electron pair; such a pair undergoes its solvation dynamics within the range of tens of picoseconds. We proposed a descriptive mechanism of the solvation in the presence of metal cations.

Explaining these solvation dynamics requires additional studies, especially through quantum chemical calculations.

Author contributions

S. D. contributions include conceptualization, data curation, methodology, validation, visualization, and writing; M. M. contributions include methodology, validation, and writing; and D. D. contributions include investigation, data curation, and visualization.

Conflicts of interest

There are no conflicts to declare.

Data availability

The dataset ''Solvation dynamics of electron–metal cation contact pairs in LiCl water salt solutions'' by S. Denisov and D. Dobrovolskii (2025) is publicly available on Zenodo at **https://doi.org/10.5281/zenodo.15234552**.

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