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Is There Any Effect of Solution Microstructure on the Solvated Electron Absorption Spectrum in LiCl/H_2O Solutions?

A. N. Asaad,[†] N. Chandrasekhar,[‡] A. W. Nashed,[§] and P. Krebs*

Institut für Physikalische Chemie, Lehrstuhl für Molekulare Physikalische Chemie, Universität Karlsruhe (TH), Kaiserstrasse 12, D-76128 Karlsruhe, Federal Republic of Germany

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Some years ago I. V. Kreitus measured changes in the optical characteristics of pulse radiolytically generated solvated electrons in solutions of LiCl in H_2O and D_2O over the LiCl concentration range 0−14.06 M (*J. Phys. Chem.* **1985**, *89*, 1987). With increasing LiCl concentration he observed a *nonuniform* blue-shift of the position of the e_{solv}^- absorption maximum and a similar *discontinuous* increase of the half-width of the absorption band. More rapid changes were observed just in those concentration regions which correspond to the stoichiometric mixtures such as $LiCl{\cdot}6H_2O$ and $LiCl{\cdot}4H_2O$, respectively. Kreitus asserted that this effect is related to the microstructure of the solutions produced by Li^+. He concluded finally that the high sensitivity of the e_{solv}^- absorption spectrum to slight microstructural changes in the medium could be used in future as a precise method for investigation of the solution structure. These experimental results and especially their interpretation have far reaching consequences. We therefore felt there is a need to repeat at least some of these measurements very carefully. It became all the more necessary as a femtosecond study on the solvation dynamics of electrons in concentrated aqueous LiCl solutions was interpreted according to the results of Kreitus. We report on our experimental results which neither corroborate the experimental data of Kreitus nor support his theoretical conclusions.

1. Introduction

Shortly after the discovery of the hydrated electron[1] the effect of dissolved inorganic salts on the optical absorption spectrum of e_{solv}^- was studied.[2] It was observed that with increasing salt concentration the maximum of the e_{solv}^- absorption spectrum shifts to higher energies. However, usually the spectral shifts have been determined by measurements in pure water and in highly concentrated solutions.[2] To get more information, Kreitus[3] studied e_{solv}^- in detail in aqueous LiCl solutions taking advantage of the high solubility and inertness of this salt. He has measured the changes of the optical absorption of pulse radiolytically produced electrons in LiCl solutions in H_2O and D_2O at 294 K over the concentration range 0−14.06 M.

The essential experimental results of this investigation are summarized in Figures 1 and 2. Figure 1 shows the position of the maximum of the e_{solv}^- absorption band, $\hbar\omega_{max}$, as a function of the molal concentration c_m of LiCl in H_2O at 294 K (we have omitted the corresponding results in D_2O). Kreitus observed a *nonuniform* blue-shift of $\hbar\omega_{max}$ with increasing LiCl concentration. He discriminated between concentration regions where $\hbar\omega_{max}$ changes slowly and two narrow concentration intervals where $\hbar\omega_{max}$ changes strongly. At low LiCl concentrations $\hbar\omega_{max}$ in D_2O is blue-shifted in comparison with $\hbar\omega_{max}$ in H_2O, whereas above $c_m = 10$ *m*, $\hbar\omega_{max}$ coincide for both H_2O and D_2O (see Figure 2 in ref 3).

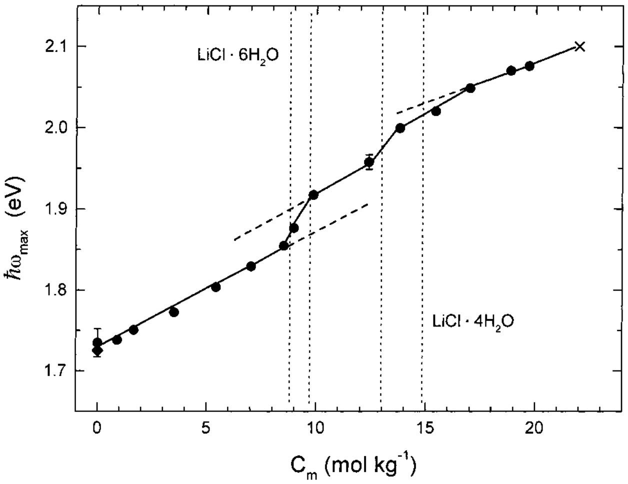

Figure 1. Shift of the absorption band maximum $\hbar\omega_{max}$ of e_{solv}^- in aqueous LiCl solutions versus molal concentration of LiCl: ●, in H_2O at $T = 294$ K, Kreitus (ref 3); ×, in H_2O at $T = 298$ K, Anbar and Hart (ref 2); ♦, in H_2O ($T = 298$ K), Jou and Freeman (ref 12). At some arbitrarily selected points we have given the maximum error mentioned by Kreitus. Note that according to Kreitus in most cases the error is within the symbol size. The vertical dashed lines sign the two narrow intervals where $\hbar\omega_{max}$ changes more rapidly with molal concentration of LiCl than in the rest of the whole concentration range (see the text and Figure 2 of ref 3).

In Figure 2 are shown the total half-width $W_{1/2}$ and the partial widths W_{low} and W_{high}, from $\hbar\omega_{max}$ to the energy at half-height on the low and high energy sides of the e_{solv}^- absorption band in the aqueous LiCl solutions obtained by Kreitus. Whereas W_{low} is almost constant, W_{high} increases with increasing amount of LiCl and shows some discontinuities in the same small concentration intervals mentioned above. It is apparent that Kreitus neglects the contradicting result of Anbar and Hart[2] (see Figure 2). In summary, this means that the addition of LiCl produces a shift of the e_{solv}^- spectra without retaining their

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* Corresponding author. E-mail: pkrebs@tchibm3.chemie.uni-karlsruhe.de.

[†] On leave from the Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt.

[‡] On leave from the Department of Chemistry, Faculty of Natural Science, Goa University, Goa, India.

[§] On leave from the Department of Materials Science, Institute of Graduate Studies and Research, Alexandria University, Alexandria, Egypt.

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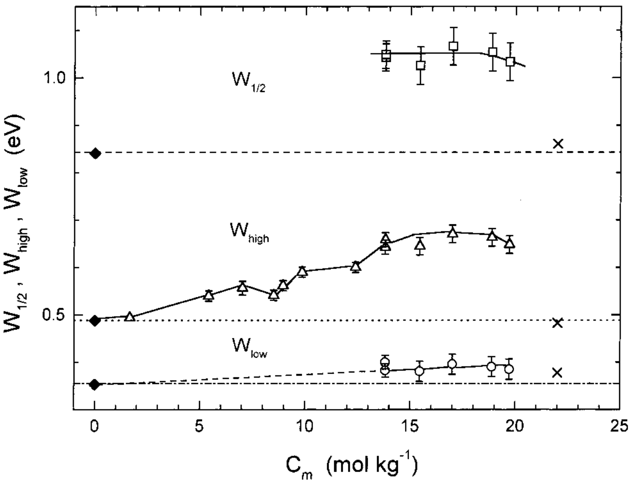

Figure 2. The total half-width, $W_{1/2}$, and the partial half-widths, W_{low} and W_{high}, of the absorption band of e_{solv}^- in aqueous LiCl solutions (T = 294 K) versus molal concentration c_m of LiCl: ○, W_{low} in H_2O; △, W_{high} in H_2O; □, $W_{1/2}$ in H_2O, Kreitus (ref 3); ×, in H_2O, Anbar and Hart (ref 2); ♦, pure H_2O at T = 298 K, Jou and Freeman (ref 12).

shape. It follows immediately from these measurements that the so-called *shape stability of the optical profile* of the solvated electron absorption band observed in different solvents and solvent mixtures[4,5] is obviously violated in these solutions.

These observations are discussed by Kreitus considering additionally the results of his photoemission experiments in aqueous LiCl solutions concerning the changes of the bottom of the conduction band, V_0, of e_{solv}^- caused by the amount of LiCl in the solution.[6] However, it is not the aim of this paper to repeat the detailed discussion of Kreitus. We want to focus rather on an essential result emphasized by Kreitus: The "hydrated" electron samples the microstructure of the LiCl/H_2O solution, especially in the small concentration intervals which correspond to the stoichiometric mixtures LiCl•6H_2O and LiCl•4H_2O respectively (see Figure 1). This interpretation is based on the concept that these solutions have a somewhat "crystalloid" structure. In other words: Kreitus tries to answer the question of whether there is sufficient free water besides the water molecules involved in the solvation of the ions in the different concentration ranges in order to solvate the electrons. He concluded for example that in the small concentration intervals water is completely consumed to build up the corresponding solvation shells of the ions and, therefore, the absorption of e_{solv}^- should show anomalies. The conclusions of Kreitus culminate in the perspective that due to the high sensitivity of the e_{solv}^- absorption spectrum against slight microstructural changes in the medium it can be used in future as a precise method for investigation of the solution structures.

As the experimental results of Kreitus have very far reaching consequences, it seems to be necessary to repeat such measurements once more carefully. Therefore, a short description of our experiments is given in section 2. In section 3 we present our experimental results which are compared with those of Kreitus. Conclusions are drawn in section 4.

2. Experimental Section

Solvated electrons were produced by irradiation of light in the low energy tail of the CTTS-spectrum of the iodide ion, I^-, according to

$$I^- + \hbar\omega \rightarrow I^\bullet + e_{solv}^- \tag{1}$$

Therefore, potassium iodide (about 2 to 5 × 10^{-3} M, Merck, suprapur 99.5%) was used in LiCl/H_2O mixtures. The wanted amount of anhydrous LiCl (Merck, p.a.) was filled in a reservoir of the sample cell (together with KI) and dried under vacuum (5 × 10^{-6} mbar) for at least 24 h. Then the cell was flushed with N_2 (Messer Griesheim 3.0) and the required amount of freshly prepared 3-fold distilled water was filled in the vessel. The concentration of LiCl was additionally controlled by weighing the sample at the different stages of preparation. The maximum error in the molal concentration was determined to be less than 0.01 mol kg^{-1}. The solutions in the cell are made free of O_2 and CO_2 by at least five freeze–pump–thaw cycles at the vacuum line. Thereafter, the sample cell with the solution (about 20 cm^3) was flushed again with about 1 bar N_2. For the measurements, the solution was then transferred to the attached spectrosil cell (Hellma) of 10 mm optical path length. The temperature was measured to be 297 ± 1 K. It should be pointed out that before the sample preparation the glass vessel with the quartz cell was cleaned with overheated water vapor for at least 12 h.

To produce e_{solv}^-, we used a Kr/F excimer laser (Lambda Physik, Compex 102: $\lambda = 248$ nm; pulse duration: 30 ns; pulse energy entering the optical cell: < 30 mJ; the laser was additionally equipped with a 90° beam profile rotation unit). The constancy of the pulse energy of the laser was always controlled by the built-in calibrated energy monitor (error ≤ 2%) in order to get a relative measure for the produced electron concentration. As a detector we used a UV-silicon-photodiode (EG&G FND 100Q). The time constant for the detecting system (with some additional electronics) is in the order of 20 ns. We have used only a single grating for the monochromator (JOBIN-YVON M25). Therefore, the experimental spectral range is limited, partially also by the sensitivity of the UV-silicon-photodiode, to $1.24 \le \hbar\omega \le 3.5$ eV. As the analyzing light source we applied a high-pressure xenon arc lamp (Osram XBO 450). To obtain a higher signal-to-noise ratio, the intensity of the lamp was pulsed up during the absorption measurement by increasing the lamp current by a factor of about 15 for 0.6 ms with the aid of a home built pulsing unit.[7] We have, of course, placed suitable filters (Schott) in front of the optical cell to stop higher order diffraction of the grating.

The concentration of e_{solv}^- was in the order of some 10^{-6} M. We observed a mean lifetime of e_{solv}^- in LiCl/H_2O at T = 297 ± 1 K of about 2–6 μs. In Figure 3 we show the absorption spectrum of a solution of 13.83 mol kg^{-1} LiCl in H_2O with 5 × 10^{-3} M KI immediately after the irradiation of a 248 nm laser light pulse. The electrons are not the only transient species absorbing light in the spectral range $1.24 \le \hbar\omega \le 3.5$ eV. We have to consider also the transient absorption of I_2^- which is formed according to

$$I^\bullet + I^- \rightarrow I_2^- \tag{2a}$$

and disappears slowly through the disproportion reaction[8,9]

$$I_2^- + I_2^- \rightarrow I_3^- + I^- \tag{2b}$$

The maxima of the I_2^- absorption bands in aqueous LiCl solutions (13.83 m) are at 1.75 ± 0.02 eV ($^2\Pi_g \leftarrow {}^2\Sigma_u^+$) with $W_{1/2} = 0.45 \pm 0.02$ eV and 3.27 ± 0.02 eV ($^2\Sigma_g^+ \leftarrow {}^2\Sigma_u^+$) with $W_{1/2} = 0.79 \pm 0.03$ eV (see Figure 3). The ratio of the extinction coefficients is obtained to be ϵ (3.27 eV)/ϵ (1.75 eV) = 3.7 ± 0.3. Within the experimental error these results are independent of the LiCl concentration. Pikaev et al.[10] mentioned absorption bands for an aqueous solution of 10^{-3} M potassium iodide alone

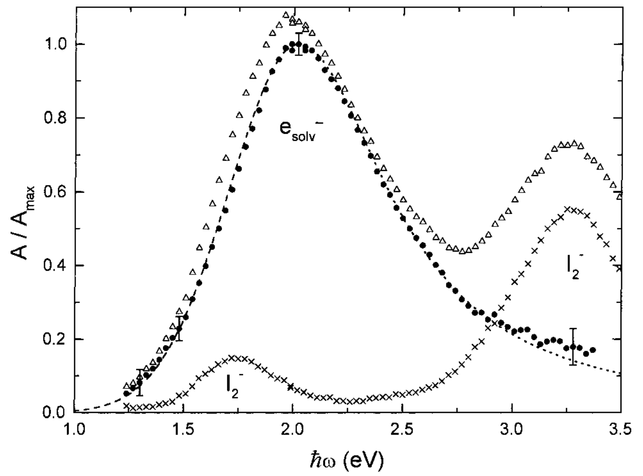

Figure 3. Optical absorption of a solution of 13.83 mol kg^{-1} LiCl in H$_2$O (5 × 10^{-3} M KI; $T = 297.5$ K) immediately after the irradiation of a 248 nm excimer laser pulse: △, total spectrum; ×, spectrum of I$_2^-$; ●, spectrum of solvated electrons. The error bars show the maximum calculated error. Pointed line: Lorentzian line shape ($W_{high} = 0.51$ eV); dashed line: Gaussian line shape ($W_{low} = 0.37$ eV); $\hbar\omega_{max} = 2.02 \pm 0.02$ eV.

at 1.71 and 3.31 eV with a half-width $W_{1/2} = 0.8$ eV for the high energy band. The corresponding ratio of the extinction coefficients was given as 3.7. In methanol at 298 K we have detected slightly shifted band positions of I$_2^-$ at 1.65 ± 0.03 eV with $W_{1/2} = 0.42 \pm 0.03$ eV and at 3.20 ± 0.03 eV with $W_{1/2} = 0.72 \pm 0.03$ eV; the ratio of the extinction coefficients was 3.03.[11] I$_2^-$ has a much longer lifetime than e$_{solv}^-$. Therefore, the overlapping spectra of I$_2^-$ and e$_{solv}^-$ are in principle easily separated to obtain the pure spectrum of e$_{solv}^-$ (see Figure 3). At each spectral energy we have averaged results over at least 6 single measurements. In general the energy interval was chosen to be 0.03 eV. Sometimes the interval was diminished to 0.015 eV near to the absorption maximum to increase the accuracy of the determination of $\hbar\omega_{max}$. The spectra are normalized to the maximum absorbance A_{max} of e$_{solv}^-$.

3. Results and Discussion

In Figure 4 we compare the normalized spectra of e$_{solv}^-$ for a low (2.51 mol kg^{-1}) and a high (13.83 mol kg^{-1}) LiCl concentration with the results of Jou and Freeman in pure water at 298 and 274 K.[12] We have fitted the absorption bands with a Gaussian line shape at the low-energy side and with a Lorentzian line shape at the high-energy side (see also Figure 3) as was done by Jou and Freeman in the case of e$_{solv}^-$ in pure water.[12] By this method we include more experimental points in the determination of $\hbar\omega_{max}$. Despite this, the maximum calculated error for $\hbar\omega_{max}$ is in the order of ± 0.02 eV,[11] whereas Kreitus pointed out that in his measurements the error in the determination of the absorption band maximum does not exceed the (exaggerated) limit of ±0.008 eV. It is apparent that the e$_{solv}^-$ spectrum for 2.51 *m* at 297 K agrees quite well with the hydrated electron spectrum at 274 K. This means that the excess electron in the 2.51 *m* aqueous LiCl solution behaves like an electron in water at lower temperatures. Our spectrum of e$_{solv}^-$ in a 13.83 *m* solution shows that the high energy half-width, $W_{high} = 0.51 \pm 0.02$ eV, is much smaller than that of Kreitus, that is, $W_{high} \approx 0.651 \pm 0.018$ eV ($W_{1/2} = 0.88 \pm 0.03$ eV has to be compared with $W_{1/2} \approx 1.045 \pm 0.03$ eV; see Figure 2).

In Figure 5 we present our $\hbar\omega_{max}$ values as a function of the molal concentration of LiCl. We observe a continuous blue-shift in the whole concentration range $0 \leq c_m \leq 22$ mol kg^{-1}.

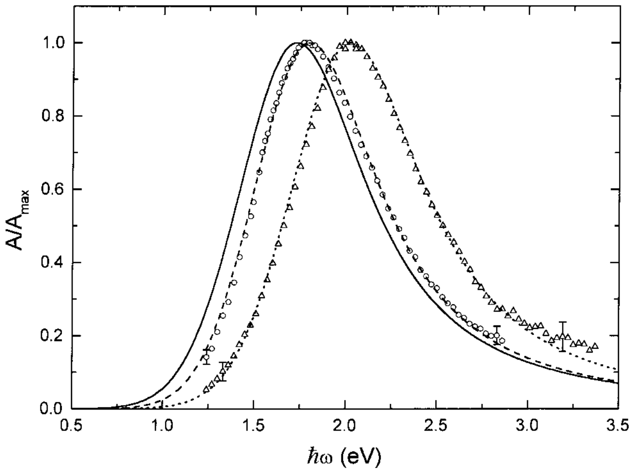

Figure 4. Absorption spectra of solvated electrons in a diluted (2.51 mol kg^{-1}, ○) and a concentrated (13.83 mol kg^{-1}, Δ) solution of LiCl in H$_2$O in comparison with the spectra of solvated electrons in pure H$_2$O at 298 and 274 K obtained by Jou and Freeman (ref 12): solid line, the best fit to the spectrum of hydrated electrons at 298 K; dashed line, the best fit to the spectrum of hydrated electrons at 274 K (see the text).

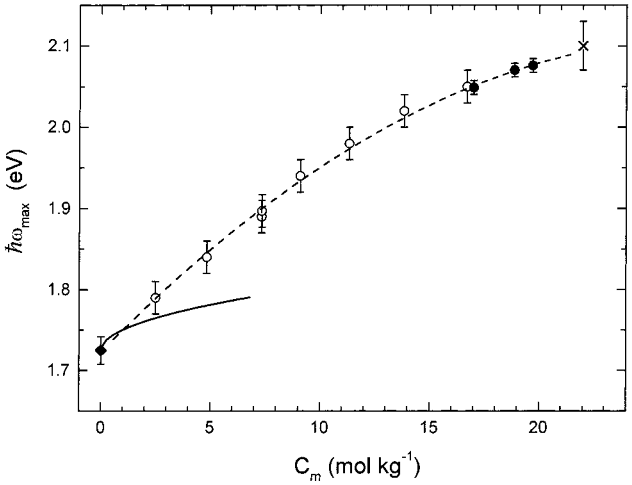

Figure 5. The position of the maximum of the absorption band of e$_{solv}^-$ in LiCl/H$_2$O solutions as a function of the molal concentration of LiCl: (○), this work. ♦, e$_{solv}^-$ in pure water at 298 K (Jou and Freeman, ref 12); ×, 15 M LiCl solution at 298 K (oversaturated), Anbar and Hart (ref 2); (●), some results of the work of Kreitus (ref 3). The dashed line serves as a guide for all the experimental results. The solid line is a theoretical estimate based on the Debye−Hückel theory (see the text and ref 26).

It should be emphasized that there are *no relevant breaks* in the blue-shift of the band maximum exceeding the experimental error. More important in our opinion are the experimentally observed half-widths of the e$_{solv}^-$ absorption band: In contrast to the findings of Kreitus the total half-width $W_{1/2}$ and the partial widths W_{low} and W_{high} do not depend essentially on the LiCl concentration (compare Figure 6 and Figure 2). The mean value of about 0.87 ± 0.03 eV for $W_{1/2}$ is comparable to that found by Jou and Freeman[12] in pure water (0.843 eV at 298 K; the standard deviation was given to be less than 0.01 eV, ref 12) and to the estimate of 0.86 eV found by Anbar and Hart[2] in an oversaturated aqueous LiCl solution (15 M at $T = 298$ K). However, it is striking that Anbar and Hart did not observe or did not mention (see Figure 1 of ref 2) the additional broad absorption band of Cl$_2^-$ with its absorption maximum at 3.65 eV which was observed by Kreitus in the solutions at all LiCl concentrations in a similar pulse radiolytic experiment. From

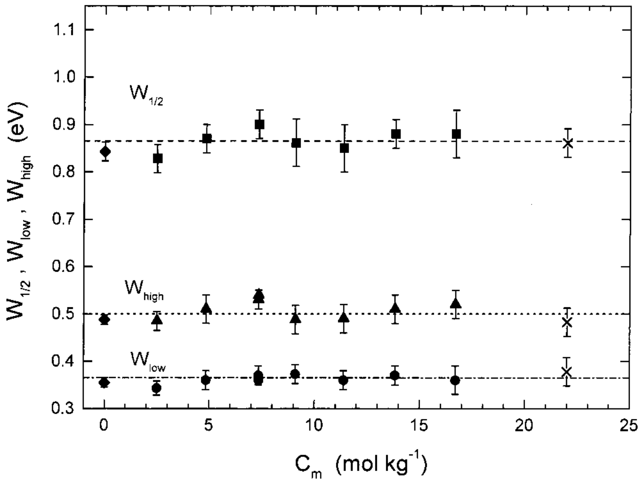

Figure 6. The different half-widths W_{low}, W_{high}, and $W_{1/2}$ of e_{solv}^- in LiCl/H_2O solutions as a function of LiCl concentration c_m: ●, ▲, ■, this work; ×, Anbar and Hart (ref 2). ♦, in pure H_2O, Jou and Freeman (ref 12). The dashed, the pointed, and the dashed-pointed lines represent the mean values of the different half-widths defined in the text. The error bars show the maximum calculated error.

our measurements it follows that within the experimental error the shape stability of the e_{solv}^- absorption band is obviously maintained in these solutions as well (see Figures 4 and 6).

Kreitus divides the concentration range of LiCl solutions in three characteristic intervals (see Figure 1). To sustain this treatment and the corresponding interpretation, Kreitus presented some additional experimental evidence from other properties of these solutions. Typical examples are the activity coefficient[13] and some NMR relaxation experiments performed by Rauhvargers et al.[14] Because our results do not agree with those of Kreitus we have to consider, of course, these additional experimental arguments. The last paper[14] is not accessible to us, but we will see below that we can rely on some excellent investigations in this field. We did not discover any anomalies of the properties of aqueous LiCl solutions. To demonstrate this fact we present in Figure 7 just the activity coefficient[13] and the ^{7}Li spin−lattice relaxation rate $(1/T_1)^{\mathrm{Li}}_{\mathrm{H_2O}}$ for aqueous LiCl solutions as a function of the molal concentration at 298 K.[15] There are no "break points" in these curves which may refer to some "crystalloid" entities in these solutions. Appart from the $c^{1/2}$ dependency of the activity coefficient at low LiCl concentrations[13] ($c_m \ll 0.25$ *m*, not visible in Figure 7) it continuously increases with increasing c_m above 0.5 *m*.

Nuclear magnetic relaxation measurements alone (spin−lattice relaxation T_1) yield important information on molecular motion and structure around the hydrated ions such as Li^+ and Cl^-. Li^+ relaxation rates in aqueous LiCl solutions, $(1/T_1)^{\mathrm{Li}}_{\mathrm{H_2O}}$, have been determined already by Craig and Richards,[16] by Woessner, Snowden, and Ostroff,[17] and by Hertz, Tutsch, and Versmold.[15] The data agree within a few percent. The strong structure forming effect of Li^+ and the weak structure breaking effect of Cl^- are well-known. Therefore, we can focus only on the Li^+ ion. From the relaxation rates it follows immediately that at low concentrations of LiCl one has $Li^+(H_2O)_4$. Of course there exists a second solvation shell. Due to the structure forming effect of Li^+, water in these solutions behaves spectroscopically and dynamically like water at lower temperatures.[18] However, this does not mean that the H_2O structure in the solution is necessarily the same as that of H_2O in pure water at low temperatures. It is apparent that our experimental results concerning e_{solv}^- agree with this statement (see Figure 4 and the text). Above concentrations of about 7 mol kg^{-1} water is completely involved in solvation shells and with increasing concentration the hydration sphere of Li^+ is destructed as it follows from quadrupolar relaxation rate measurements on Li^+.[15] With increasing concentration the quadrupolar relaxation caused by the first hydration shell increases due to the breakdown of cubic symmetry of $Li^+(H_2O)_4$. Just the relaxation due to quadrupole interaction represents the largest contribution to $(1/T_1)^{\mathrm{Li}}_{\mathrm{H_2O}}$. This means that on the way to the highest concentration the H_2O molecule no longer knows which Li^+ ion it belongs to. There is finally a disordered mixture of the species Li^+, Cl^-, and H_2O. From the translational diffusion it follows that one observes with increasing LiCl concentration the transition from the electrolyte solution with "hydrated" ions to the melt.[15] In principle $(1/T_1)^{\mathrm{Li}}_{\mathrm{H_2O}}$ does not show any peculiarities. However, it is to be expected that for $c_m \leq 2$ mol kg^{-1} the $^7Li^+$ magnetic relaxation rate in H_2O shows a behavior similar to the $c^{1/2}$ dependency in D_2O (at low concentrations the molar concentration c becomes approximately equal to c_m).[19]

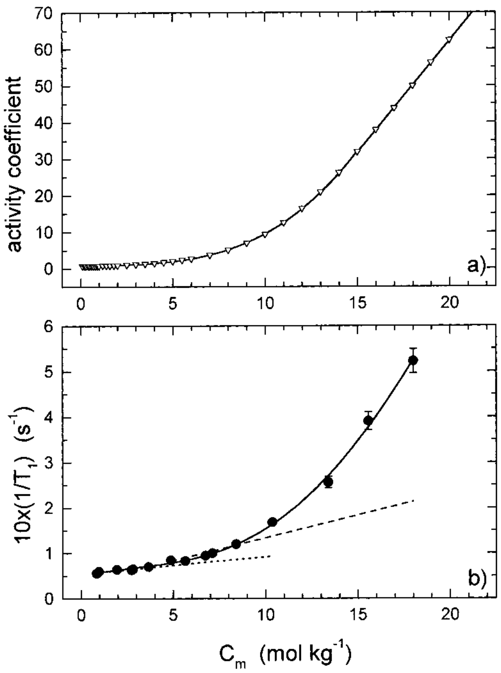

Figure 7. (a) Activity coefficient of aqueous LiCl solutions as a function of the molal LiCl concentration c_m at 298 K (see ref 13). (b) ^{7}Li spin−lattice relaxation rates in aqueous LiCl solutions as a function of the molal LiCl concentration c_m at 298 K (see refs 15, 17).

Finally, we do not want to withhold the result of Woessner et al. They have presented some evidence for the occurrence of structural rearrangements at distinct concentrations. In their measurements in the LiCl concentration range $0.5 \leq c_m \leq 7$ mol kg^{-1} they found a change of $(1/T_1)^{\mathrm{Li}}_{\mathrm{H_2O}}$ at a concentration between 4 and 4.5 molal LiCl. In our opinion this interpretation is due to a somewhat artificial evaluation of the experimental data in the *reduced* concentration range $c_m \leq 7$ mol kg^{-1} (see Figure 1 in ref 17). We are convinced that Woessner et al. would not have evaluated their experimental data as shown in Figure 7 had they known at that time the relaxation rates for $c_m \geq 7$ mol kg^{-1}.

Because there is a transition from an electrolyte to the corresponding melt we need, besides this detailed knowledge on aqueous LiCl solutions, also some information on excess electrons in melts of alkaline halides (*F*-centers) in order to discuss our experimental results. Due to experimental difficulties such as corrosion of the optical windows in systems like $Li_x(LiCl)_{1-x}$, up to now there have been no reliable absorption spectra of electrons in LiCl melts.[20] Young estimated $\hbar\omega_{max} = 2.25$ eV at $T = 923$ K.[21] Pikaev et al.[10] report on spectra of pulse radiolytically produced electrons in LiBr melts (but not in LiCl melts). At $T = 873$ K they observed $\hbar\omega_{max} = 2.48$ eV and $W_{1/2} = 1.50$ eV. With increasing T, $\hbar\omega_{max}$ is shifted to the red. Excellent measurements on the system $Na_x(NaBr)_{1-x}$ performed by Nattland, Rauch, and Freyland[22] at $T = 1073$ K yield $\hbar\omega_{max} = 1.62$ eV and $W_{1/2} = 1.09$ eV. Such small half-widths are found too in other melts of alkaline halides.[23] Therefore, it is concluded that in the case of LiBr the half-width $W_{1/2}$ found by Pikaev et al. is obviously too large. In summary, from all these results it follows that for electrons in aqueous LiCl solutions one should observe a blue shift of $\hbar\omega_{max}$ with increasing LiCl concentration. For increasing c_m we have an increasingly disordered mixture of Li^+, Cl^-, and H_2O. We think that in such solutions there exists a sufficiently high concentration of suitable "traps" to solvate the excess electron after some reorganization of the surrounding water molecules and the ions. In principle one should observe a transition from a solvated electron state to an *F*-center. However, the experimental proof of this transition ends at the saturation of the solution.

Lakhno and Vasil'ev[24] have estimated the dependence of the solvated electron's absorption band shift on the ionic strength of an aqueous LiCl solution for $c_m \leq 7\ m$. For this purpose they generalized the theory of Debye and Hückel developed for heavy charged particles to describe the properties of localized electrons in a dilute solution of a strong electrolyte. The electron is regarded as Pekar's polaron[25] although it is well-known that the polaron in itself is a very imperfect model for the solvated electron.[26] The result of this calculation is given in Figure 5. Theory predicts $d^2(\hbar\omega_{max})/dc_m^2 < 0$ which is rather in agreement with our results than with those of Kreitus.

The solvation dynamics of excess electrons in concentrated aqueous LiCl solutions ($c_m \leq 11\ m$) has been investigated also by a femtosecond study in comparison with the formation of e_{solv}^- in pure water by Gauduel and co-workers.[27] Keeping in mind the results of Kreitus these authors concluded that a favorable spatial distribution of deep traps created by the presence of the stable counterion Li^+ would represent a specific order of the liquid for an ultrafast *direct* electron capture in the electronic ground state. The time constant of this process (Gauduel and co-workers called it the "dynamics of electron localization") is about 100 fs and is independent of the LiCl concentration (see Figure 5 of ref 27). On one hand, the probability to find a solvent configuration which corresponds just to that of an *equilibrated* solvated (localized) electron should be very small. On the other hand the proposed process should depend on the Li^+ concentration if the above given suggestion is valid. In addition, Gauduel and co-workers observed a second channel for the electron hydration (instead of hydration one should rather say solvation) with a concentration dependent relaxation time constant of about 500 fs for $c_m \approx 11\ m$. Keeping in mind the results of a recent femtosecond study on the formation of the hydrated electron in pure water by Hertwig, Hippler, Unterreiner, and Vöhringer[28] and finally the results of the present investigation then the work of Gauduel and co-workers has to be reinterpreted.

4. Conclusions

In summary, the influence of a *large* amount of LiCl ($c_m \approx 22$ mol kg^{-1}) on the spectral shift of the absorption maximum in the order of $\Delta\hbar\omega_{max} \approx +0.38$ eV is relatively small. For example, a blue shift of $\Delta\hbar\omega_{max} \approx +0.26$ eV is observed for the hydrated electron by simply decreasing the temperature of pure water from 380 to 274 K.[12] In this temperature range $W_{1/2}$ decreases slightly from 0.88 to 0.828 eV. From the total continuous shift of $\Delta\hbar\omega_{max} \approx +0.38$ eV observed in this investigation it follows that the spectrum of e_{solv}^- is comparatively *insensitive* to the microscopic properties of the LiCl solution. By the application of optical sum rules on the absorption spectra it follows immediately that the probability distribution of the electron in the saturated LiCl solution becomes more compact than in pure water.[29] Strictly speaking, the mean dispersion in position of the solvated electron, $\langle r^2 \rangle$, for $c_m \approx 22$ mol kg^{-1} is about 4.9 ± 0.4 Å^2 in comparison with 5.94 ± 0.36 Å^2 in pure water at 298 K.[30] Obviously, solvated electrons in an extremely wide variety of aqueous media (this work and ref 5) are to be regarded as indeed hydrated electrons.

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(30) $\langle r^2 \rangle$ determines the equilibrium radial probability density $\rho(r) = (3/2\pi\langle r^2 \rangle)^{3/2} \exp\{-3r^2/2\langle r^2 \rangle\}$ of the solvated electron about its mean position.