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Hydrated Electron Extinction Coefficient Revisited

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The extinction coefficient of the hydrated electron $(e^-)_{aq}$ generated by pulse radiolysis is evaluated relative to the methyl viologen radical cation $^{\bullet}MV^+$, whose extinction coefficient at 605 nm has been carefully measured in the past. We find that the room temperature $(e^-)_{aq}$ extinction coefficients reported in the literature are underestimated by 10−20%. We obtain $\epsilon = 22\,700$ M^{-1} cm^{-1} for the 20 °C hydrated electron at 720 nm, assuming the $^{\bullet}MV^+$ extinction is 13 700 M^{-1} cm^{-1} at 605 nm. This has implications both for second-order reaction rate measurements of $(e^-)_{aq}$ and for the estimate of its integrated oscillator strength.

I. Introduction

Playing a major role in radiolysis, photochemistry, and electron-transfer reactions in aqueous solution,[1,2] the hydrated electron, $(e^-)_{aq}$, has been an interesting and important object for study since its first spectroscopic observation in 1963.[3] Its broad absorption band centered near 720 nm at room temperature and its high extinction coefficient have made it a useful tool for studying the chemistry of other species.[4] To use $(e^-)_{aq}$ for dosimetry, and to study second-order recombination reactions, its molar extinction coefficient, $\epsilon_{e^-}(\lambda)$ must be known precisely. The precise value of $\epsilon_{e^-}(\lambda)$ also has implications for the study of $(e^-)_{aq}$ itself, as it is needed to determine the total oscillator strength of the hydrated electron spectrum. For many years, the preferred value was[5] $\epsilon_{e^-}(720) = 18\,600$ M^{-1} cm^{-1} but more recently Elliot and Ouellette[6] revised this upward to ca. 20 000 M^{-1} cm^{-1}.

In the process of measuring $\epsilon_{e^-}(\lambda)$ at elevated temperature in pressurized water, we have remeasured its value at room temperature relative to that of the methyl viologen radical cation.[7] The result described below is higher by 10−20% over all previous reports.

II. Experimental Section

The electron pulse radiolysis system used has been described previously.[8] Briefly, 2 ns pulses from an 8 MeV linear accelerator were used to create aqueous radical concentrations of ~1 μmol L^{-1} per pulse. A pulsed 75 W Xe lamp was used for probe light. Wavelength selection was achieved with 10 nm bandpass filters, and a digital oscilloscope recorded transient signals from the silicon photodiode detector.

The dichloride salt of methyl viologen (MV^{2+}) was obtained from Sigma and used as received. Solutions of $\sim 1 \times 10^{-4}$ M MV^{2+} were made with water from a ASTM type I water purification system. Both the MV^{2+} solution and a bottle of deionized water were bubbled with argon. Concentrations of MV^{2+} were varied in the sample cell by changing the relative flow rates from the two bottles. The temperature during all experiments was kept at 20 ± 1 °C.

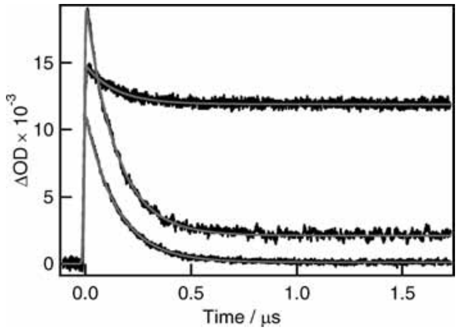

Figure 1. Transient absorption in Ar-saturated MV^{2+} solution at 600, 720, and 850 nm, in order of decreasing long time offset. Gray lines are from global fits to the data. By 850 nm, there is less than 1% absorption from $^{\bullet}MV^+$.

III. Results

Transient absorption of the pulse-irradiated 1×10^{-4} M MV^{2+} solution was recorded between 440 and 1000 nm. Typical traces are shown in Figure 1. At 720 nm, the absorption decreases with a lifetime of several hundred nanoseconds to a small offset, which remains constant over the course of several microseconds at low doses. At 600 nm, a much smaller decay to a larger constant offset is observed. Above 850 nm, the initial signal decays to baseline. The decay time constant at all wavelengths between 440 and 1000 nm is the same. The prompt submicrosecond decay at all wavelengths between 440 and 1000 nm is due to $(e^-)_{aq}$ scavenging by MV^{2+}:

$$(e^-)_{aq} + MV^{2+} \rightarrow {}^{\bullet}MV^{+} \qquad (1)$$

The constant final offset at all wavelengths below ~850 nm is due to $^{\bullet}MV^+$ absorption. At higher doses, the long time offset begins to decay with a dose-dependent lifetime. This decay is attributed to second-order chemistry between $^{\bullet}MV^+$ and other radiolytic products. H atom and OH radical adducts can be observed by absorption at 470 nm at longer times (>10 μs).[9–11]

The $(e^-)_{aq}$ extinction coefficient may be determined from the relative amplitudes of the decays measured at the peak absor-

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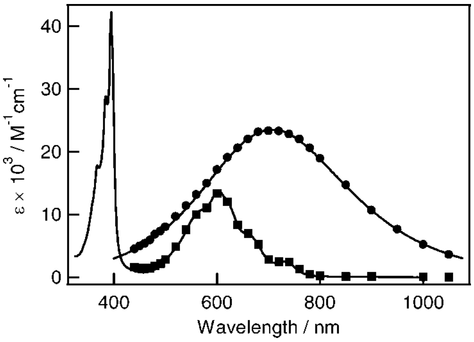

Figure 2. Spectra recovered from fit amplitudes for $(e^-)_{aq}$ (circles) and for MV^{2+} (squares) in Ar-saturated water. Also shown is the measured steady state spectrum of $^{\bullet}MV^+$ and calculated spectrum of $(e^-)_{aq}$ from ref 15 (solid lines). All traces have been scaled to give ϵ = 13 700 M^{-1} cm^{-1} at 605 nm for $^{\bullet}MV^+$.

bances for the relevant species, 720 and 605 nm. The amplitudes were determined by globally fitting to the following function:

$$A(t) = A_0 e^{-t/\tau} - A_1(e^{-t/\tau} - 1) \qquad (2)$$

where A_0 is the amplitude of the $(e^-)_{aq}$ decay, A_1 is the amplitude of the $^{\bullet}MV^+$ rise, and τ is the lifetime of the $(e^-)_{aq}$. Including spur recombination of the hydrated electron[12] in the fit of the 720 nm trace does not significantly change the quality of the fit or the resulting amplitudes.

The rate of reaction of MV^{2+} with $(e^-)_{aq}$ was determined to be $(6.2 \pm 0.7) \times 10^{10}$ M^{-1} s^{-1} from pseudo-first-order kinetics with changing MV^{2+} concentration, in good agreement with previous results.[7,10,13] The spectra of the $^{\bullet}MV^+$ radical and $(e^-)_{aq}$ were determined from decay traces at wavelengths from 440−1000 nm. Reconstructed spectra from the globally fit amplitudes are shown in Figure 2. Both spectra agree well with previous reports.[7,14,15]

The relatively low spectral resolution of the filters means that the variation of the absorption spectra over their bandpass needs to be carefully considered. We measured the spectrum of $^{\bullet}MV^+$ in a spectrophotometer after irradiating a solution of 1×10^{-4} M MV^{2+} and 1×10^{-2} M ethanol in a sealed, N_2-purged cuvette (lower solid line in Figure 2). We measured the transmission bandpass of our filters using the same lamp-filter combination as in our pulse radiolysis measurements, but with a monochromator at the focus, rather than a photodiode. The fwhm of the 600 and 720 nm filters were both 10 nm (measured with 1.5 nm resolution).

Because the amplitudes used in the determination of $\epsilon_{e^-}/\epsilon_{MV+}$ were unconstrained in the fitting, we compared the ratio of the fitted amplitudes for $(e^-)_{aq}$ and $^{\bullet}MV^+$ at 720 and 600 nm to the steady state spectra, appropriately integrated over the filter bandwidths. For $^{\bullet}MV^+$ we calculate ϵ_{MV+}(720 nm)/ϵ_{MV+}(600 nm) to be 0.194. From our fitted transients, we obtain a ratio of 0.19 ± 0.02 (1σ). For $(e^-)_{aq}$, the spectral ratio ϵ_{e^-}(720 nm)/ϵ_{e^-}(600 nm) = 1.42.[14,15] From the fitted transients, we calculate 1.40 ± 0.08. This agreement gives us confidence that our overall fitting procedure is returning accurate amplitudes.

Integrating the steady state $^{\bullet}MV^+$ spectrum over the bandpass of the 600 nm filter gives an average absorbance 1.6% lower than the (high resolution) value at 605 nm. After applying the 1.6% correction to the measured amplitude of $^{\bullet}MV^+$ at 600 nm, we find the ratio of ϵ_{e^-}(720 nm)/ϵ_{MV+}(605 nm) to be 1.66 ± 0.04 (1σ).

To obtain an absolute extinction coefficient for $(e^-)_{aq}$ from this experiment we must have an absolute extinction coefficient for $^{\bullet}MV^+$. Watanabe and Honda[7] published a careful study of the $^{\bullet}MV^+$ spectrum in 1982, and found that for concentrations below 1×10^{-4} M of methyl viologen, ϵ_{MV+} = 13 700 ± 200 M^{-1} cm^{-1} at the broad 605 nm maximum. Although this number has been widely accepted, Buxton and Wood[16] in 1989 insisted a better estimate is 13 100 M^{-1} cm^{-1}. The basis for Buxton and Wood's argument is the comparison of pulse radiolysis *G* values (yields) for $^{\bullet}MV^+$ from a study of Mulazzani et al.[17] and for $Fe(CN)_6^{3-}$ in a study of Schuler et al.[18] However, in 1995 it was shown[19] that the dosimetry used in the earlier papers was incorrect. After correction of the dosimetry, the numbers agree within error, and there is no need to adjust the $^{\bullet}MV^+$ extinction coefficient.

We accept the $^{\bullet}MV^+$ extinction coefficient of ϵ_{MV^+}(605 nm) = 13 700 ± 200 M^{-1} cm^{-1} measured by Watanabe and Honda.[7] Then, using the ratio measured in our experiment, the value of ϵ_{e^-}(720) is 22 700 ± 500 M^{-1} cm^{-1} (1σ) at 20 °C. This number also agrees with our independent experiments based on simultaneously measuring the $(e^-)_{aq}$ transient absorption and scavenging product concentration. The latter experiments will be described in a more extensive publication.[20]

IV. Discussion

Most previous reports of the hydrated electron extinction coefficient have been based on pulse radiolysis/transient absorption measurements of the product $G\epsilon_{e^-}(\lambda)$, which is determined by standardization of the measured absorption (A = dose × G × ϵ) against a "known" dosimeter $G\epsilon$, where G is yield. Calculation of $\epsilon_{e^-}(\lambda)$ from $G\epsilon_{e^-}(\lambda)$ requires, in addition to precision of the radiation pulses, a correct G value. Our methodology in this work is fundamentally different, in that we directly track the conversion of "all" $(e^-)_{aq}$ into $^{\bullet}MV^+$ radicals and require no knowledge of radiation dose or yield.

Of the earlier reports of the hydrated electron extinction coefficient, the most convincing (and most utilized) was the careful study of Fielden and Hart,[5] who arrive at ϵ_{e^-}(720) = 18 600 M^{-1} cm^{-1}. It was difficult for us to believe their result could be in error by 22%. These authors used pulse radiolysis with a very small dose/pulse and a multipass White cell to measure $G\epsilon_{e^-}$(720 nm) for $(e^-)_{aq}$ at pH 13 in H_2-saturated water. Absolute yields (G) were determined separately in pH 13 solutions of $KMnO_4$ from the MnO_4^{2-} radical, whose extinction coefficient is known. The individual G values measured for the OH, H, and $(e^-)_{aq}$ radicals in this study are essentially those accepted today, so the only plausible explanation is error in the actual transient absorbance of $(e^-)_{aq}$ in the multipass cell. At this late date it is impossible to decide what might have gone wrong. Perhaps the number of passes was actually greater than 16.

In 1972 Jha, Bolton, and Freeman[21] reported a value of ϵ_{e^-}(720 nm) = 18 900 ± 600 M^{-1} cm^{-1} using a $G(e^-_{aq})$ of 2.8 × 10^{-7} mol/J and dosimetry using O_2-saturated thiocyanate. They took $G\epsilon$ = 2.3 × 10^{-4} m^2 J^{-1} for the thiocyanate dosimeter. However, Buxton and Stuart[19] later corrected this value to 2.59 × 10^{-4} m^2 J^{-1}, which, when applied to Jha et al.'s calculation, revises their ϵ_{e^-}(720 nm) to 21 300 M^{-1} cm^{-1}. The size of this correction is indicative of the true degree of uncertainty in many free radical extinction coefficients measured in the 1970s and 1980s.

The most recent literature determination of $\epsilon_{e^-}(\lambda)$ was by Elliot and Ouellette,[6] who in 1994 reported a value of ϵ_{e^-}(720) = 20 000 ± 700 M^{-1} cm^{-1}. Their measurement was reportedly based on the thiocyanate dosimeter using a $G\epsilon$ of 2.48 × 10^{-4} m^2 J^{-1}. Although they knew of the corrected thiocyanate dosimeter result of Buxton and Stuart,[19] and cited the unpublished work, it appears that a miscommunication regarding units resulted in the use of an incorrect number.[22] In later work found in AECL reports,[23] Elliot and Stuart corrected the error in dosimetry and obtained a value of $\epsilon_{e^-}(720) = 21\,000$ M^{-1} cm^{-1}. This number is in good agreement with Jha et al.[21] as corrected above but is still 8% lower than our result. It suggests that the $G\epsilon$ value of the thiocyanate dosimeter might need further revision.

V. Conclusion

A simple experiment directly comparing transient absorption of the hydrated electron with that of the methyl viologen cation radical shows that the $(e^-)_{aq}$ extinction coefficient has been underestimated in the past by 10−20%. The correct value is $\epsilon_{e^-}(720) = 22\,700 \pm 500$ M^{-1} cm^{-1} (1σ) at 20 °C. An increase in the value of $\epsilon_{e^-}(\lambda)$ will have several consequences. Second-order recombination rate constants determined using the $(e^-)_{aq}$ absorption will be low by 10−20%, because k/ϵ is the parameter actually measured. The compilation of free radical rate constants used to model chemistry in reactors or nuclear waste environments will need to be modified.[24–27] A similar 10−20% error will be found wherever $(e^-)_{aq}$ itself is used for dosimetry or quantum yield measurement. For example, femtosecond yields of $(e^-)_{aq}$[28,29] and indole radicals[30,31] following 2-photon ionization of water may need to be re-evaluated. Hydrated electron quantum yields recently measured for excimer-laser excitation of aqueous anion CTTS bands are all 10% high.[32] The increase in $\epsilon_{e^-}(\lambda)$ will also have an effect on the $(e^-)_{aq}$ oscillator strength (f) and other quantities estimated from the integration of its absorption spectrum.[33–35] The most recent estimate of f for $(e^-)_{aq}$ by Jou and Freeman yielded a value of 0.76.[14,36] Using their fitting functions and parameters, but our revised $\epsilon_{e^-}(720)$, we calculate $f = 0.85$.

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