

On the Existence of Dielectrons $[(e_2^-)_{aq}]$ in Aqueous Solution

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Summary The existence of long-lived dielectrons in aqueous solutions is questioned, due to the very low absorption found in solutions where $(e_2^-)_{aq}$ is supposed to exist; the upper limit for the extinction coefficient of $(e_2^-)_{aq}$ in this system, in the range 600–1100 nm, is only several units.

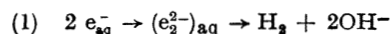
order to explain the magnetic properties of concentrated solutions of alkali metals in liquid ammonia.¹ These data were later interpreted² as being due to M^- .

The pair of electrons and the dielectrons were formed in two other matrices: (i) in KCl crystals the F and F' centres were observed³ and (ii) in irradiated 10 M-NaOH glasses at $T < 130K$ both the paramagnetic electron and the diamagnetic dielectrons were observed.⁴

THE possible formation of dielectrons was suggested in

In aqueous solutions there was no direct evidence for the

existence of $(e_2^-)_{aq}$, though it might be expected to be an intermediate in the well known reaction:



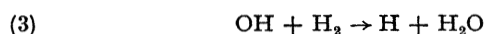
In reaction (1) the hydride ion may be an alternative intermediate to the $(e_2^-)_{aq}$. The lifetime or identity of none of these intermediates has yet been proved or determined.

Recently Basco, Kenney, and Walker⁵ through an elegant double flash-photolysis experiment on an H_2 -saturated alkaline aqueous solution, provided evidence for $(e_2^-)_{aq}$ with a lifetime of *ca.* 0.1 s.

Their first flash through the absorption of light in the u.v. region produced the solvated electron by the reaction:



followed by



and



The solvated electron was followed by its absorption at 633 nm and decayed with $\tau_{1/2} > 50 \mu s$ according to reaction (1).

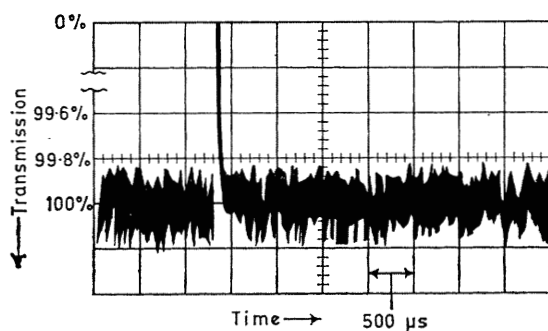


FIGURE. Absorption signal at 900 nm. Argon-saturated aqueous solution of 10^{-2} M-isopropyl alcohol + 10^{-3} M-NaOH. The fast trace is the decay of e_{aq}^- .

After the e_{aq}^- decay was over, a second flash was delivered to the solutions. This flash passed through a filter and contained only wavelengths where OH^- does not absorb. The second flash regenerated the e_{aq}^- , as observed by its absorption at 633 nm. This second flash was assumed to initiate the reaction:



We decided to re-examine this system where e_{aq}^- was generated by pulse radiolysis and $(e_2^-)_{aq}$ supposed to be formed thereafter through reaction (1). The details of the pulse radiolysis techniques are described elsewhere.⁶

In our experiments we irradiated argon-saturated alkaline solutions with 10^{-2} M-alcohols; the solutions were made with triple-distilled water. All reagents were of analytical grade. The decay of e_{aq}^- was followed at wavelengths from 600 to 1100 nm with an R196 photomultiplier and appropriate filters in front of it in order to eliminate

scattered light at lower wavelength passing through the monochromator. In all experiments scattered light was found to be negligible (except that for 1100 nm it was about 10%).

The initial concentrations of e_{aq}^- produced by the pulse were about 1.5×10^{-5} M, and the decay was essentially second-order with lifetimes of about 6 μs (when smaller pulses were employed with initial concentrations of e_{aq}^- *ca.* 10^{-6} M the lifetime of e_{aq}^- was 40–50 μs in solutions containing ethanol or isopropyl alcohol and 80–100 μs in methanolic solutions). These lifetimes indicate the purity of the water used. In order to determine whether the stable end-products of the radiolysis react considerably with e_{aq}^- , we measured $\tau_{1/2}$ of e_{aq}^- with a small pulse [where $(e_{aq}^-)_0$ *ca.* 1 μM] before and after a big pulse [where $(e_{aq}^-)_0$ *ca.* 15 μM] and found a decrease in $\tau_{1/2}$ of less than 15%.

We measured the absorptions of the solutions after e_{aq}^- decayed (at times of 10^{-4} – 10^{-2} s after the pulse). Any absorption left should be due to $(e_2^-)_{aq}$ being formed, according to earlier determination from reaction (1),⁵ and having a lifetime of about 0.1 s.

At 200 μs after the pulse (e_{aq}^- decays to about 10^{-9} M; during the first 20 μs it decays mainly through reaction (1), and thereafter by reactions with H_2O_2 , with aldehydes formed by the radiation and with the water and traces of impurities.

In all experiments there was practically no absorption left at 1 ms after the pulse (Figure); at this time, e_{aq}^- has decayed already and $(e_2^-)_{aq}$ should still be stable.⁵ In the Table the extinction coefficients for the $(e_2^-)_{aq}$ are given in the systems investigated.

These values are upper limits, due to the line-width of the trace. (These values are calculated with the assumption that only part of the e_{aq}^- decayed by reaction (1), while the rest reacted with impurities, radiation products, or with the other radicals such as CH_2OH . If we assume that all e_{aq}^- undergo reaction (1) the values in the Table would be even smaller.)

TABLE

Upper limit for the extinction coefficients of $(e_2^-)_{aq}$

λ (nm)	10^{-2} M-Pr ⁱ OH + 10^{-3} M-NaOH ^{ab}	10^{-2} M-EtOH + 5×10^{-2} M- NaOH ^{ab}	10^{-2} M-MeOH + 10^{-3} M-NaOH ^{ac}
600	7		
700	3		
900	3	3	1.5
980			4.5
1050	15		6.0
1100	15		

^a These ϵ values were calculated assuming that only 60% of e_{aq}^- gave $(e_2^-)_{aq}$ via reaction 1.

^b These ϵ values were measured after 200 μs .

^c These ϵ values were measured after 2 ms.

We believe that the very low extinction coefficients found at the time when e_{aq}^- decayed and $(e_2^-)_{aq}$ is supposed to be stable put some serious doubts on the existence of a long-lived $(e_2^-)_{aq}$ as recently suggested.⁵ Our doubts are based on the expected spectra of $(e_2^-)_{aq}$ and on the possibility of its photodecomposition by the second flash in the experiments described.⁵

Our hesitation does not rule out the possibility of the existence of $(e_2^-)_{aq}$, but does call into question its stability as a relatively long-lived species.

Another argument against a long-lived $(e_2^-)_{aq}$ is based on the known precursors of H_2 . H_2 is formed at least partially in spurs through reaction (1). Efficient e_{aq}^- scavengers are known to decrease $G(H_2)$ at concentrations above 1 mM. If $(e_2^-)_{aq}$ is formed in the spurs in reaction (1) and lives 0.1 s it would diffuse out of the spurs, and yield H_2 long after it is homogeneously distributed in the bulk of the solution. The fact that only concentrations above 1 mM of e_{aq}^- scavengers cause a decrease in $G(H_2)$ forces us to assume that $(e_2^-)_{aq}$ is very unreactive with all of these scavengers [the rate constants of $(e_2^-)_{aq}$ with these scavengers should be less than $10^8 \text{ M}^{-1} \text{ s}^{-1}$]. This assumption would be very surprising.

If we compare the spectra of e_{aq}^- and $(e_2^-)_{aq}$ in alkaline glasses or the F and F' centres we can make an estimate of the spectrum of $(e_2^-)_{aq}$ in aqueous solutions. Kevan⁷ calculated the red shift of the $(e_2^-)_{aq}$ spectrum due to

temperature change assuming a similar T -dependence to that shown by the spectrum of e_{aq}^- . From this, one finds that the extinction coefficient of $(e_2^-)_{aq}$ at 1100 nm should exceed $3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at room temperature. Our results show a value which is lower by more than two orders of magnitude. Similar values are calculated from the F' centres.

From our measured values of ϵ_λ for $(e_2^-)_{aq}$ we cannot see how Basco *et al.*⁵ could have had enough light to regenerate the e_{aq}^- in reaction (5).

An experiment which would be helpful to elucidate this problem would be pulse-radiolysis of a solution where reaction (1) occurs, followed after a delay of several ms by photolysis of this solution with an i.r. laser pulse from a Nb laser. This would be a variation of the experiment of Basco *et al.*,⁵ but under more favourable conditions.

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⁷ L. Kevan, personal communication.