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Hydrated electron in subcritical and supercritical water: a pulse radiolysis study

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Abstract

Temperature dependences of the e_{aq}^- spectrum and $G\varepsilon_{max}$ were investigated by the pulse radiolysis method over a temperature range of 25–400°C including the supercritical condition and the e_{aq}^- formation in supercritical water (D_2O) was confirmed. With increasing temperature, the absorption peak (λ_{max}) of e_{aq}^- shifts significantly to longer wavelength. The value of $G\varepsilon_{max}$ in supercritical water is considerably smaller than in liquid water at room temperature. The behavior of e_{aq}^- revealed here is helpful for an extensive understanding of water radiolysis and for the study of e_{aq}^- involving radical reactions in supercritical water. © 2000 Published by Elsevier Science B.V.

1. Introduction

Since physical properties of supercritical water (> 373°C, > 221 atm) differ greatly from those of room temperature water, e.g. the dielectric constant of supercritical water could be as lower as that of nonpolar organic compounds, the knowledge of radiation induced processes in supercritical water is basically important for a thorough understanding of water radiolysis. In reactor chemistry, the study of radiolysis of supercritical water is indispensable for the evaluation of radiation induced corrosion in the future generation of nuclear reactors. It has been

shown that operating efficiency and profitability of commercial nuclear reactors can be increased remarkably if high temperature water presently used in the primary cooling loop is replaced by supercritical water [1]. More over, radicals generated by radiation can be employed to investigate the kinetics of chemical reactions occurring in supercritical water oxidation, because supercritical water can be utilized as a benign medium for waste oxidation, biomass processing and many other practical applications [2]. Indeed, there have been recently reports on oxidation of halogenated phenolates [3] by OH and aminobenzoates [4] by CO_3^- in supercritical water studied with the pulse radiolysis technique. Additionally, the study of water radiolysis under near- and supercritical conditions is also of great theoretical interest for diffusion-kinetic modeling [5,6] and theoretical consideration of e_{aq}^- spectrum [7,8].

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The study of e_{aq}^- is a part of our project aiming for understanding of radiation induced chemical reactions in supercritical water since e_{aq}^- is one of the most important radiolytic products and it can be scavenged by many species to form new radicals. Temperature effects on e_{aq}^- have been extensively studied using the pulse radiolysis technique and the absorption maximum of e_{aq}^- spectrum is found to shift to longer wavelength with increasing temperature. The highest temperatures investigated are usually at 100–300°C [9–13], not exceeding the critical temperature of water. Although there was one report [14] on the e_{aq}^- spectrum at temperatures up to 390°C below the critical pressure, the information provided is very limited. It is fundamentally important to verify the e_{aq}^- formation and study its behavior in detail for obtaining unambiguous information of e_{aq}^- in supercritical water. In the present experiment, we investigated the temperature effect on e_{aq}^- spectrum at 25–400°C including supercritical conditions by pulse radiolysis.

2. Experimental

A high temperature irradiation cell (from Jasco) made of Hastelloy C273 was used for the experiment and its structure is illustrated in Fig. 1. The cell can withstand temperatures up to 500°C and pressures up to 500 atm. It has an internal volume of 0.4 ml and is equipped with three sapphire windows for optical access. Two sapphire windows perpendicular to the electron beam allow the access of analyzing light through an aperture ($\phi = 3$ mm) and the light path length is 15 mm. The sapphire window opposite to the electron window can be used for access of laser beam in case of laser photolysis. Thickness of the window was trimmed to 2 mm for obtaining high absorbed dose.

Water is loaded from a reservoir by a HPLC pump (Jasco) and preheated in a coiled stainless tube ($\phi = 0.15$ mm) before flowing into the cell. Water exiting the cell is cooled down and then drained after passing through a pressure regulator, by which back

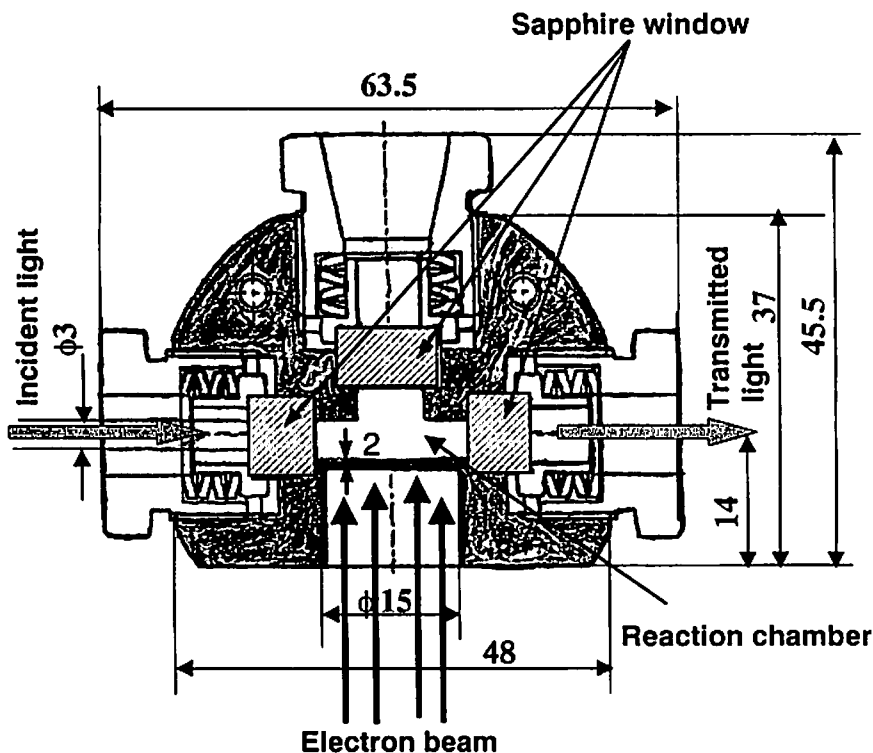


Fig. 1. Cross section of the high temperature cell for pulse radiolysis. Size unit is in mm.

pressure in the system can be conveniently adjusted. The cell is heated up in a heater which is run under a program operation. Two thermocouples are used to monitor temperatures in the outside and inside of the cell. A pulsed lamp, two monochromators, and two photodiodes (Hamamatsu S1722-02 and G3476-05) were used in the detection system for measurement of absorption in UV-visible and infrared regions, respectively. The detector signal was amplified and then digitized and averaged on a digital oscilloscope (Tektronix TDS380P) which was connected to a computer. Normally an averaging of 3–4 pulses was applied to obtain reliable signal under supercritical conditions.

Because light water (H_2O) strongly absorbs infrared light at wavelength longer than 1100 nm, heavy water (D_2O) with a purity of 99.9% (Aldrich) was employed throughout the experiment at 25–400°C and additional experiments with H_2O at 25–200°C under otherwise identical conditions were performed for comparison. A continuous purge of the saturating Ar gas was maintained through the pump reservoir throughout the experiment. The flow rate of water was 4–5 ml/min, corresponding to a residence time of 5–6 s. Pulse duration was 100 ns. The dose per pulse at room temperature was determined using N_2O -saturated 1.0×10^{-2} M KSCN solutions (H_2O) and a $\text{Ge}(\text{SCN})_2^-$ of 5.2×10^{-4} m²/J at 475 nm [15]. Absorbed doses were corrected for density changes with temperature and calculated for D_2O system after electron density correction. The pulse-to-pulse variation was monitored by a current detector placed behind the cell.

3. Results and discussion

3.1. Absorption spectra and E_{max}

Fig. 2a shows time profiles of e_{aq}^- in D_2O at 1100 nm in the range 25–400°C. It is demonstrated that e_{aq}^- is formed under all the applied conditions, though the absorption intensity and decay rate of e_{aq}^- vary with condition. Since the temperature and pressure applied for curve e are beyond the critical point of D_2O (371°C, 216 atm) [16], we conclude that e_{aq}^- is formed in supercritical water despite the consider-

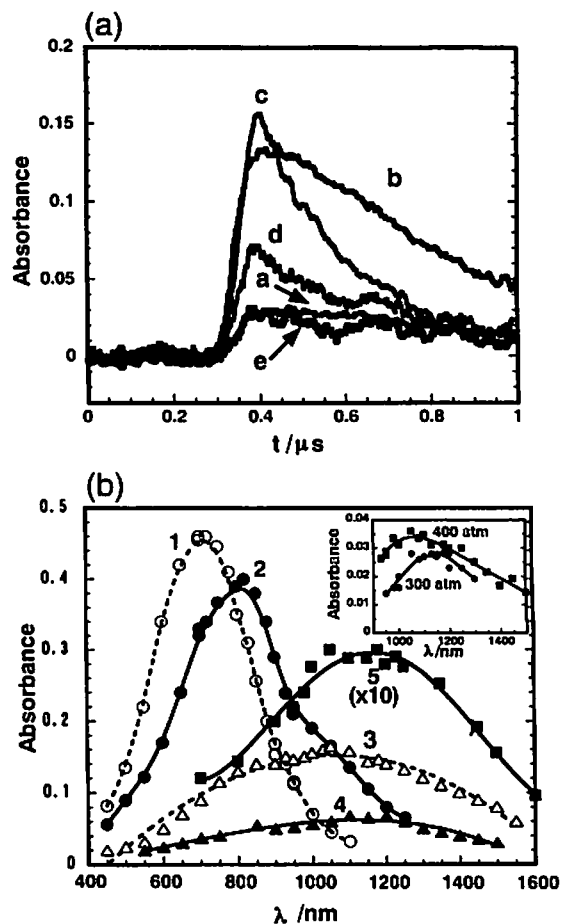


Fig. 2. (a) Time profiles of e_{aq}^- at 1100 nm in D_2O . 46 Gy/pulse. a. 25°C, 1 atm; b. 100°C, 100 atm; c. 250°C, 200 atm; d. 350°C, 250 atm; e. 400°C, 350 atm. (b) Absorption spectra of e_{aq}^- . Conditions for curves 1–5 are the same as for curves a–e in (a). Inset: Spectra of e_{aq}^- at 400°C under pressures of 300 and 400 atm.

able decrease in degree of hydrogen bonding [17] and dielectric constant. The formation of e_{aq}^- in supercritical H_2O was also confirmed at 1100 nm. The e_{aq}^- decay increases with temperature up to 300°C and then decreases with temperature at 350°C and 400°C. The e_{aq}^- decay above 100°C can be fitted better by a first-order plot than a second-order, consistent with the report of Elliot and Quелlette [18].

Absorption spectra of e_{aq}^- obtained at the end of pulse are shown in Fig. 2b. The spectra are described without correction of e_{aq}^- decay during the pulse and without normalization with density. It is clear that

absorption band becomes broader and absorption maximum λ_{\max} shifts to longer wavelength with increasing temperature. For example, λ_{\max} shifts from 700 nm at 25°C (1 atm) to 1040 nm at 250°C (200 atm) and to 1200 nm at 400°C (350 atm). The red shift of absorption band is indicative of the shallower potential well for e_{aq}^- at high temperatures. A previous study [19] has shown that, at a given temperature, λ_{\max} increases with decreasing pressure. The pressure effect should be more pronounced in supercritical water because a small change of pressure causes a great change in water density. Such an example is the blue shift of λ_{\max} with pressure at 400°C, as shown in the inserted figure.

Fig. 3 shows the energy of absorption maximum, E_{\max} , plotted as a function of temperature. As is seen, there is an excellent agreement among the data of different groups from room temperature to 200°C, with a temperature coefficient of -3×10^{-3} eV/°C [12]. However, a discrepancy appears as temperature is further increased. In the higher temperature region, our values are in good agreement with Christensen and Sehested [12] but larger than those of Michael et al. [14] and Gaathon et al. [20]. The difference between our value at 400°C and that of Michael et al.

at 390°C [14] is about 0.2 eV, corresponding to a shift of λ_{\max} from 1200 to 1400 nm. We consider this great difference caused by the pressure difference. This is because even a small change of pressure may result in a large variation in density, dielectric constant and other physical properties, which in turn lead to a shift of λ_{\max} . Although the actual pressure is not given in the report of Michael et al., it seems to be much lower than the critical pressure by considering the pressure dependence of e_{aq}^- spectrum shown in the inset of Fig. 2b in this work. Above consideration is not contradictory to the report [20] that E_{\max} in D_2O vapor is 0.88–1.02 eV at 250–345°C.

Mechanisms of the red shift of λ_{\max} with temperature are not clear. Even a complicated simulation [21] failed to exhibit such phenomenon. The shift of λ_{\max} depends on the change of solvent environment. Decreases of H-bonding, dielectric constant (ϵ) and density with temperature should be, at least partly, responsible for the red shift. A linear correlation of E_{\max} with the product of ϵ and density was obtained [22] previously in a narrow temperature range. Inset of Fig. 3 shows a good linear relationship of E_{\max} with ϵ for temperature from 25°C to 400°C. This correlation is consistent with the blue shift of λ_{\max} with increasing pressure at constant temperature, considering the pressure effect on ϵ .

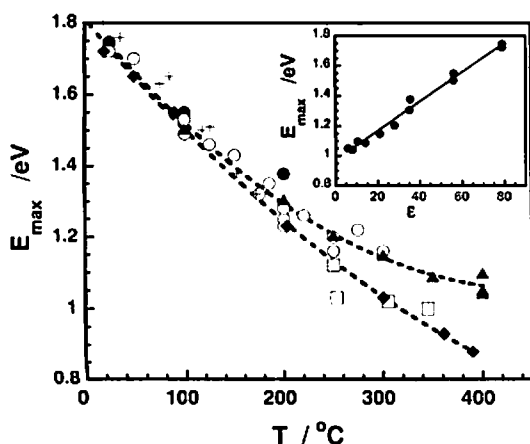


Fig. 3. Correlation of E_{\max} with temperature for e_{aq}^- . □ D_2O (Ref. [20]), ♦ D_2O (Ref. [14]), ○ H_2O (Ref. [12]), + D_2O (Ref. [10]), ▲ D_2O (this work, conditions shown in Fig. 2), ● H_2O (this work, 200 atm). Dashed lines are smoothed with data of us and Ref. [14], respectively. Inset: Correlation of E_{\max} with dielectric constant using our data.

3.2. $G\epsilon_{\max}$ of e_{aq}^-

Since the present work is inadequate to determine temperature effect on either $G(e_{\text{aq}}^-)$ or $\epsilon(e_{\text{aq}}^-)_{\max}$, the product $G\epsilon_{\max}$ is used for the evaluation of temperature effect. Fig. 4 shows a decrease of $G\epsilon_{\max}$ with temperature in our work. This is very different from other workers [11–14] who observed slightly increased or unchanged $G\epsilon_{\max}$ with increasing temperature. At present, only the temperature dependence implied in D_2O at 19–172°C [10] is similar to ours, but these authors simply attributed it to the e_{aq}^- decay during the pulse. Since our work was carried out in neutral water and the previous work [12] was performed in alkaline water under high pressure of H_2 , we suggest that the initial pH of solution probably plays an important role in temperature dependence of $G\epsilon_{\max}$. In the presence of pressurized

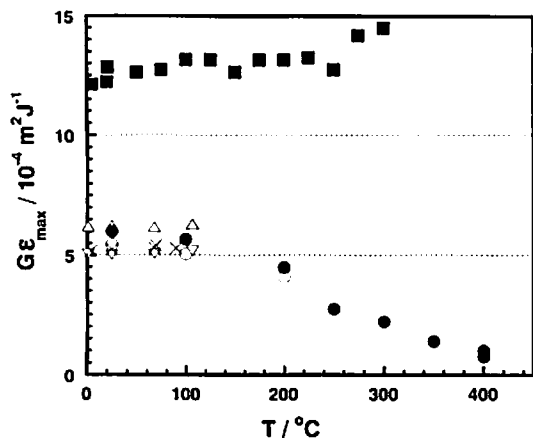


Fig. 4. Temperature dependence of $G\epsilon_{\max}$ for e_{aq}^- ■ H_2O (pH = 12, $[\text{H}_2] = 0.12\text{--}0.2$ M, Ref. [12]); × H_2O (pH = 9.5, Ref. [14]); △ D_2O & ▽ H_2O (Ref. [11]); ● D_2O & ○ H_2O (this work).

H_2 , H is formed through the reaction of $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$. In alkaline solution, H can be converted to e_{aq}^- by reacting with OH^- and thus the reaction of e_{aq}^- with H^+ is suppressed, leading to a slower e_{aq}^- decay and a higher e_{aq}^- yield as compared with neutral water. More important is the high acidity of water at high temperature. Value of pH in water could be decreased by 1–2 units [23] at high temperatures, i.e. an increase of $[\text{H}^+]$ by 1–2 orders. The high concentration of H^+ will lead to a fast decay of e_{aq}^- . The high dose per pulse of about 50 Gy, applied in this work is probably another major factor involving the low $G\epsilon_{\max}$. As pointed out by Shiraishi et al. [13], the e_{aq}^- decay becomes faster at higher dose per pulse and the dose dependence is more effective with increasing temperature. Dose dependence of the e_{aq}^- decay was similarly observed at 200°C by others [18]. The e_{aq}^- decay during the pulse is not significant in our work because the pulse duration is 100 ns and the lifetime of e_{aq}^- is much longer even in supercritical water.

Change of either $G(e_{\text{aq}}^-)$ or ϵ_{\max} with temperature is not surprising as one considers the remarkable red shift and changes in water property with temperature. It has been found that ϵ_{\max} decreases [18] and $G(e_{\text{aq}}^-)$ increases [13,24] slightly with temperature in the pulse radiolysis experiments. The e_{aq}^- yield was found [25] to increase with temperature up to 250°C for irradiation with γ -rays and fast neutrons. At

higher temperatures, the yields determined in γ -radiolysis are scattering, e.g. very different values of 0.39 [26] and 0.04 [27] $\mu\text{mol/J}$ at 300°C and 400°C, respectively, are reported. However, it is necessary to point out that the assumption of temperature independence of absorption peak and absorption coefficient for the e_{aq}^- adduct in pulse radiolysis seems inappropriate and the product analysis without blank test in γ -radiolysis is sometimes problematic because of thermal instability at high temperatures. More accurate determination of $G(e_{\text{aq}}^-)$ is required for high temperatures especially above 200°C.

Like its effect on E_{\max} , the decrease of ϵ may result in a decrease of $G(e_{\text{aq}}^-)$ at high temperatures especially in supercritical water. According to the Onsager formula [28], the probability of an electron escaping from its geminate positive ion to become free is equal to $\exp(-r_c/r)$, where r is the distance at which the electron becomes thermalized and r_c is the Onsager distance given by $r_c = e^2/(4\pi\epsilon_0\epsilon kT)$, in which e is the electronic charge, ϵ_0 is the permittivity in vacuum, ϵ is the relative dielectric constant, k is Boltzmann constant and T the absolute temperature. The ϵ of water decreases from 79 at 25°C (1 atm) to 8 at 400°C (350 atm), corresponding to an increase of r_c from 0.7 to 3.1 nm. Compared to room temperature, smaller fraction of electrons escape at 400°C and more electrons may recombine with positive ions before diffusing out of the spur, leading to a decrease of the e_{aq}^- yield.

Although many factors affect $G(e_{\text{aq}}^-)$ and $G\epsilon_{\max}$ in the high temperature region, we tend to believe that the e_{aq}^- yield or ϵ_{\max} in supercritical water is smaller than in ambient liquid water. This is because the $G\epsilon_{\max}$ in supercritical water (400°C) is only about 1/7 of that at room temperature, such a significant decrease is difficult to be explained by the above mentioned reasons without assuming a very small $G(e_{\text{aq}}^-)$ or ϵ_{\max} in supercritical water. More work is still in progress to examine this.

Acknowledgements

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