NOTES

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A Solvated Electron Formed from the Water by the Irradiation of the Recoil Particles of ^{10}B(n,α)^{7}Li and ^{6}Li(n,α)T

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Synopsis. The G values of a solvated electron produced by ionizing radiation from the (n,α) activation of boron and lithium were estimated to be 0.36 ($\pm$0.06) and 0.50 ($\pm$0.05) in neutral aqueous solutions ($ClCH_2COOH$–N_2O), and 0.24 ($\pm$0.05) and 0.46 ($\pm$0.05) in alkaline aqueous solutions ($K_3Fe(CN)_6$–NaOH), respectively.

The dependence of the radical yield in irradiated aqueous solutions on the LET (linear energy transfer) of the radiation has been actively investigated.[1–2)] In water radiolysis, the free radical yields decrease and the molecular yields increase with an increase in the LET of the radiation. This effect is believed to be due to an increasing combination of radicals in the spurs and tracks as the density of radicals along the tracks increases.

However, only a few data have been reported[2)] regarding the yield of solvated electrons in water irradiated by the radiations of high LET. In this paper, we will report some data obtained with high LET radiations from the ^{10}B(n,α)^{7}Li and ^{6}Li(n,α)T reactions. Neutral aqueous monochloroacetic acid–nitrous oxide and alkaline aqueous potassium ferricyanide solutions were selected as reaction systems suitable for this purpose.

Experimental

The experiments were carried out in the thermal neutron facility (E-2) of the nuclear reactor at Kyoto University.

The thermal neutron flux, as measured by an Al-Au wire, was in the range from 1.8×10^{10} to 8.6×10^{10} n cm^{-2} s^{-1}, depending upon the exact position of the sample. The flux of the fast neutrons was relatively small. The dose rate of the γ-ray background was measured with a Fricke dosimeter. Each experiment was repeated at least 6 times; the coefficient of variation was less than $\pm10\%$.

To determine, in the first instance, whether the presence of boric acid, sodium borate, or lithium sulfate affected the reactions of the solvated electron in irradiated $ClCH_2COOH$–N_2O and alkaline $K_3Fe(CN)_6$ solutions, some experiments using ^{60}Co γ-rays were carried out; these experiments confirmed that they cannot compete significantly with the other solutes for solvated electrons in the range of concentrations using here.

The pH of the $ClCH_2COOH$-N_2O system was adjusted with NaOH. All the chemicals used were of a reagent grade. The N_2O was purified by several distillations on a vacuum line, prior to introduction into the irradiation vessel containing the degassed solution. The amount of N_2O in the solution was determined by the measurement of the pressure drop after the solution had stood for about 24 hr at room temperature.

The irradiation vessels were cleaned with boiling nitric acid and then triply rinsed with distilled water. Eight-ml portions of solutions containing ^{10}B or ^{6}Li were sealed in a silica tube.

The aquopentacyanide ions were spectrophotometrically determined by the method using NaN_3.[3)] The presence of boric acid or sodium borate and lithium sulfate did not interfere with those measurements.

Results and Discussion

Neutral Aqueous Monochloroacetic Acid–Nitrous Oxide Solutions. The yield of solvated electrons can be estimated in neutral aqueous monochloroacetic acid–nitrous oxide solutions. The pertinent reactions to be considered are:

$$e_{aq}^- + ClCH_2COO^- \longrightarrow Cl^- + CH_2COO^- \quad (1)$$

$$e_{aq}^- + N_2O \longrightarrow N_2 + O^- \quad (2)$$

$$\begin{aligned} H + ClCH_2COO^- &\longrightarrow H_2 + ClCHCOO^- && (3)\\ &\searrow Cl^- + CH_2COO^- + H^+ && (4)\\ OH + ClCH_2COO^- &\longrightarrow H_2O + ClCHCOO^- && (5)\\ &\searrow Cl^- + R\ (R;\ \text{radical}) && (6) \end{aligned}$$

Dainton and Peterson[4)] have investigated the γ-radiolysis of aqueous N_2O solutions and shown that this solute has a relatively high reactivity to the solvated electrons, leading to the formation of nitrogen (Reaction 2). Hydrogen atoms, on the other hand, react very slowly with N_2O. This system, therefore, is a useful one for the determination of the yield of solvated electrons. In fact, Eq. (7) has been confirmed by the present authors in their γ-ray experiment with 1×10^{-3} M $ClCH_2COOH$–8×10^{-3} M (or higher concentrations) N_2O at pH=6.5.[5)] In the system studied here, the value of $G(N_2)$ calculated from the dose of the γ-ray background in the nuclear reactor was 2.8, consistent with that obtained from the γ-ray irradiation.

$$G_{e_{aq}^-} = G(N_2) \quad (7)$$

Figures 1 and 2 show the relationship between the amounts of N_2 of [B] or [Li], where [B] and [Li] denote the concentrations of $Na_2B_4O_7$ and Li_2SO_4, respectively.

The G values of the solvated electrons were calculated from Eqs. (8) and (9):

$$^{B}G_{e_{aq}^-} = \frac{(N_2)}{[B]\sigma_B\phi tE_0(B)\gamma} \times 100 \quad (8)$$

$$^{Li}G_{e_{aq}^-} = \frac{(N_2)}{[Li]\sigma_{Li}\phi tE_0(Li)} \times 100 \quad (9)$$

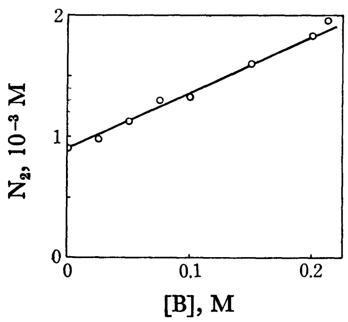

Fig. 1. Relationship between amount of nitrogen formed and concentration of boron.
Thermal neutron flux: 8.6×10^{10} n cm^{-2} s^{-1}
Irradiation time: 135 min
Initial concentration:
1.0×10^{-3} M $ClCH_2COOH$–2.6×10^{-2} M N_2O
pH: 6.0 B: $Na_2B_4O_7$

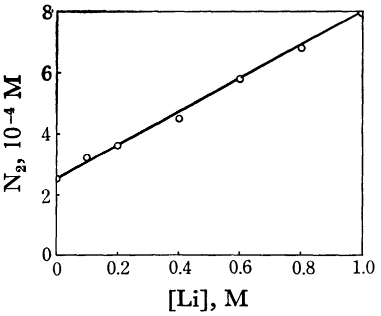

Fig. 2. Relationship between amount of nitrogen formed and concentration of lithium.
Thermal neutron flux: 1.8×10^{10} n cm^{-2} s^{-1}
Irradiation time: 300 min
Initial concentration:
1.0×10^{-3} M $ClCH_2COOH$–2.4×10^{-2} M N_2O
pH: 6.0 Li: Li_2SO_4

The boron absorption cross-section, σ_B, is taken as 755×10^{-24} cm^2.[6] The average energy absorbed by the solution from the heavy-particle recoils, $E_0(B)$, is taken as 2.35×10^6 eV per nuclear event. The lithium absorption cross-section, σ_{Li}, is taken as 71×10^{-24} cm^2, and $E_0(Li)$, as 4.78×10^6 eV.[7] Thus, from the slope of the curve, ${}^{B}G_{e_{aq}^-}$ and ${}^{Li}G_{e_{aq}^-}$ were estimated to be 0.36 (±0.06) and 0.50 (±0.05) respectively.

Alkaline Aqueous Solution of Potassium Ferricyanide. In order to secure further evidence of the yield of solvated electrons, the study was extended to another system, the $K_3Fe(CN)_6$–0.1 M NaOH solution. In this system, attention was directed toward the reaction of e_{aq}^- with $Fe(CN)_6^{3-}$.

It has been reported that aquopentacyanide is formed *via* the following competitive reaction:

$$e_{aq}^- + Fe(CN)_6^{3-} \longrightarrow Fe(CN)_6^{4-} \qquad (10)$$
$$\searrow Fe(CN)_5OH_2^{3-} + CN^- \qquad (11)$$

Then, in the range from 5×10^{-3} M to 1×10^{-2} M $Fe(CN)_6^{3-}$, Eq. (12) was confirmed:[8]

$$G_{e_{aq}^-} \simeq 2G(Fe(CN)_5OH_2^{3-}) \qquad (12)$$

where the yield of aquopentacyanide was determined by using the NaN_3 method.[3]

Figures 3 and 4 show that the relation of the yield of the aquocomplex to [B] or [Li] is linear. Thus, the radiolytic yield of the aquocomplex formed by the recoil particles was obtained from the slopes.

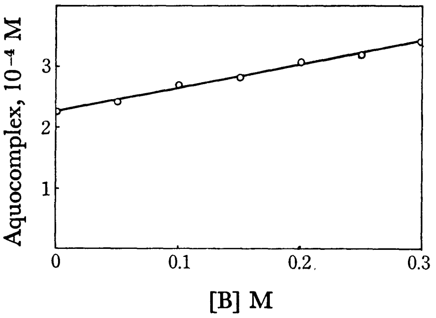

Fig. 3. Relationship between amount of aquocomplex formed and concentration of boron.
Thermal neutron flux: 5.1×10^{10} n cm^{-2} s^{-1}
Irradiation time: 52 min
Initial concentration:
5.0×10^{-3} M $Fe(CN)_6^{3-}$–0.1 M NaOH
B: $Na_2B_4O_7$

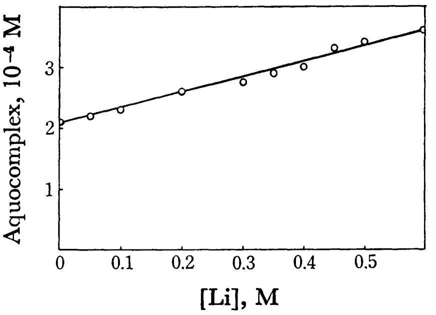

Fig. 4. Relationship between amount of aquocomplex formed and concentration of lithium
Thermal neutron flux: 5.6×10^{10} n cm^{-2} s^{-1}
Irradiation time: 64 min
Initial concentration:
5.0×10^{-3} M $Fe(CN)_6^{3-}$–0.1M NaOH
Li: Li_2SO_4

By applying the yield of the product to Eq. (12), ${}^{B}G_{e_{aq}}$ and ${}^{Li}G_{e_{aq}}$ can be estimated to be about 0.24 (±0.05) and 0.46 (±0.05), respectively.

The difference in the yields between the systems of the neutral aqueous potassium ferricyanide solutions, though small, might be caused by the difference in pH.

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