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Radiolytic organics in γ-ray irradiated aqueous solution of *N*,*N*-diethylhydroxylamine

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Abstract *N*, *N*-diethylhydroxylamine (DEHA) is a novel salt-free reducing agent used in separating Pu and Np from U in the reprocessing of spent nuclear fuel. In this paper, we report the study on γ-radiolysis of DEHA in water and its radiolytic liquid organics by gas chromatography. The radiolysis rate of DEHA increases with the absorbed dose, but decreases with the primary DEHA concentration at 0.1–0.5 mol·L^{-1} irradiated to 10–1000 kGy. The main organics produced in radiolysis of DEHA are acetaldehyde, acetic acid and ethanol. The concentration of acetaldehyde increases with the primary DEHA concentration and the absorbed dose at ≤500 kGy, but over 500 kGy it decreases with increasing dose. The dependence of the concentration of acetic acid on the absorbed dose is similar to that of acetaldehyde, with a lower turning point of the dose, though. The ethanol concentration changes differently among the irradiated samples of different primary DEHA concentrations, and this is discussed. The maximum concentrations of acetaldehyde, acetic acid and ethanol are 0.029, 0.014 and 0.028 mol·L^{-1}, respectively.

Key words *N*, *N*-Diethylhydroxylamine, γ-radiolysis, Liquid organics, Reprocessing of spent fuel

1 Introduction

In the PUREX process of treating the spent nuclear fuel (SNF), U(VI) and Pu(IV) are coextracted, by 30% TBP in kerosene, into the organic phase from the aqueous nitric acid solution, while the other fission products retain in the aqueous phase. Pu(IV) is subsequently separated from U(VI) by selectively reducing it to Pu(III), which is stripped into the aqueous phase with hydrazine stabilized U(IV) or ferrous sulfamate. As the holding reductants, hydrazine and sulfamate are the destroyer of trace nitrous acid, which initiates the oxidation of Pu(III).

However, because U(IV) is much less extractable than U(VI), a large excess of reducing agent required for acceptable amount of plutonium separation[1,2], would increase U loss into the Pu product. Also, in the ferrous sulfamate, the excessive reducing agent would increase the volume of radioactive wastes. In addition, the inorganic sulfamate and hydrazine cannot be extracted appreciably from an aqueous phase to a TBP phase, hence their failure to destroy nitrous acid rapidly, which causes re-oxidation of Pu(III) in the TBP phase[1].

The Np content in SNF increases with burnup of the nuclear fuel[3]. Fe(II) and U(IV) cannot control Np valence, causing the Np to go to different streams. *N*,*N*-diethyl-hydroxylamine (DEHA) can quickly reduce Pu(IV) and Np(VI) to Pu(III) and Np(V)[1,4,5], which are unextractable by TBP, while organic DEHA can be extracted to the TBP phase, so as to destroy the nitrous acid and stabilize Pu(III) and Np(V) in the TBP phase, hence the separation of Pu and Np from U.

Organics is usually sensitive to radiation. Previously, we conducted aqueous solution of 0.1–0.5 mol·L^{-1} DEHA irradiated to 10–1000 kGy[6–9], and found that the radiation-induced gaseous products

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were mainly hydrogen, methane, ethane and ethene, with the volume fraction of hydrogen being much higher than the other gases. We also analyzed the organics in irradiated aqueous DEHA solution by gas chromatography equipped with FFAP capillary column and flame-ionization detector[10], and found that there were DEHA, acetaldehyde, acetic acid and ethanol in irradiated DEHA solution. In this paper, we report the dependences of their concentrations on the absorbed dose and the primary DEHA concentration.

2 Materials and methods

2.1 Sample preparation and irradiation

DEHA was supplied by China Institute of Atomic Energy, in purity of 98.6 %. Aqueous DEHA solutions of 0.1, 0.2, 0.3 and 0.5 mol·L^{-1} were prepared with de-ionized water. The 4-mL solution was placed into 7-mL penicillin bottle, sealed with rubber and aluminum. These samples were irradiated to 10, 50, 100, 500 and 1000 kGy, the absorbed doses were monitored by dichromate dosimeters.

2.2 Main equipment and accessories

The samples were irradiated to 10, 50, 100, 500 and 1000 kGy in a ^{60}Co γ-ray source of 3.6×10^{15} Bq was at Shanghai Institute of Applied Physics, Chinese Academy of Sciences. GC900A gas chromatograph was from Shanghai Ke Chang Chromatograph Instruments Co., Ltd. FFAP capillary column (30 m×0.25 mm×0.25 μm) was from Dalian Institute of Chemistry and Physics, Chinese Academy of Sciences.

3 Results and Discussion

3.1 The radiolysis of DEHA

Gas chromatography was used for quantitative analysis of residual DEHA in the irradiated aqueous DEHA solution. The residual DEHA contents in the irradiated solution with dilute amount of the primary DEHA concentrations of 0.1, 0.2, 0.3 and 0.5 M are shown in Fig.1. It can be seen that for all the four samples, the residual DEHA content decreases with increasing doses, but the decrease is slower for higher primary DEHA concentrations. This means that the radiolysis rate of DEHA, i.e. the difference of the initial and residual DEHA concentrations over initial DEHA concentration, increases with the dose, but decreases with the primary DEHA concentration. At 1000 kGy, the DEHA radiolysis rate of the four samples (in primary DEHA concentration of 0.1, 0.2, 0.3 and 0.5 M) is 92%, 78%, 53% and 25%, respectively. This indicates that radiation stability of the DEHA aqueous solution can be improved by increasing the primary DEHA concentration.

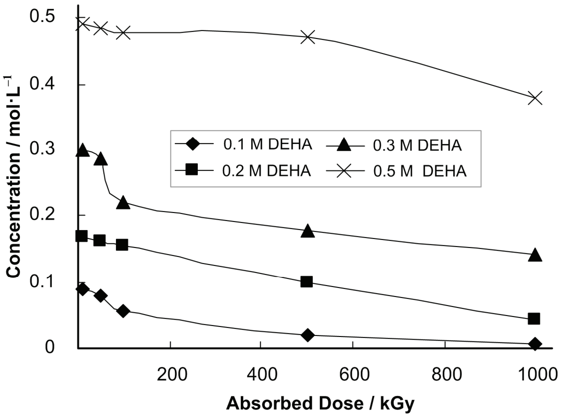

Fig.1 The residual DEHA content in the irradiated solutions of different primary DEHA concentrations.

When a dilute organic aqueous solution is irradiated, the chemical changes are mainly brought about by reactions between the active species from radiolysis of water and solute[11,12]. Under ionizing irradiation, as shown in Eq.(1), active species such as $\dot{H}$, $\dot{O}H$ and e_{aq}^- are produced in the water of DEHA solution.

$$H_2O\rightarrow \dot{H} + \dot{O}H + e_{aq}^- + H_2 + H_2O + H\dot{O}_2 + H^+ \quad (1)$$

The amount of active species of $\dot{H}$, $\dot{O}H$ and e_{aq}^- increases with the dose, and their reactions with DEHA increases, too, hence the decreased DEHA concentration with increasing doses. On the other hand, at the same dose point, the amount of the active species in the solution is constant, and so is the amount of DEHA reacted with the active species. This is why the radiolysis rate of DEHA decreases with increasing primary DEHA concentrations.

3.2 Liquid organics produced by the radiolysis of DEHA solution

The main organics in the irradiated DEHA solution are DEHA, acetaldehyde, acetic acid and ethanol.

Fig.2 shows the acetaldehyde concentration in the irradiated aqueous DEHA solutions of 0.1–0.5 $mol{\cdot}L^{-1}$. The acetaldehyde concentration increases with primary DEHA concentration. It also increases with the dose at low doses of upto 500 kGy, where it begins to decrease with increasing dose.

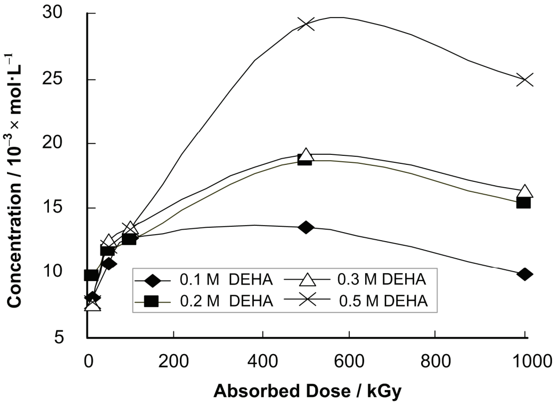

Fig.2 Acetaldehyde concentration in aqueous DEHA solutions of 0.1–0.5 $mol{\cdot}L^{-1}$ irradiated to different doses.

The acetaldehyde was mainly produced by reactions of DEHA with the $^{\cdot}OH$ and $^{\cdot}H$ generated by radiolysis of water[10]:

$$H^{\cdot} + (C_2H_5)_2NOH \rightarrow H_2 + (C_2H_5)_2NO^{\cdot} \qquad (2)$$

$$^{\cdot}OH + (C_2H_5)_2NOH \rightarrow H_2O + (C_2H_5)_2NO^{\cdot} \qquad (3)$$

$$2(C_2H_5)_2NO^{\cdot} \rightarrow CH_3CH{=}\underset{\overset{\downarrow}{O}}{N}CH_2CH_3 + (C_2H_5)NOH \qquad (4)$$

$$CH_3CH{=}\underset{\overset{\downarrow}{O}}{N}CH_2CH_3 \xrightarrow[H^+]{H_2O} CH_3CHO + C_2H_5NHOH \qquad (5)$$

With higher primary DEHA concentration, the concentration of diethyl nitroxide radical increases (Eqs.(2) and (3)), hence the increased acetaldehyde concentration with the primary DEHA concentration (Eqs.(4) and (5)).

From Eq.(1), the $H^{\cdot}$ and $^{\cdot}OH$ concentrations increase with the dose. And the concentration of diethyl nitroxide radical increases with the $H^{\cdot}$ and $^{\cdot}OH$ concentrations, hence the increased concentration of acetaldehyde with the dose.

However, when the dose is high enough, the generated acetaldehyde may react with $^{\cdot}OH$, $H^{\cdot}$ and e_{aq}^{-} to form acetic acid or ethanol, as shown in Eqs.(6)–(8).

$$^{\cdot}OH + CH_3CHO \xrightarrow{R'} CH_3COOH \qquad (6)$$

$^{\cdot}R$: radical which can react with $H^{\cdot}$.

$$^{\cdot}H + CH_3CHO \xrightarrow{RH} CH_3CH_2OH \qquad (7)$$

$$e_{aq}^{-} + CH_3CHO \xrightarrow{RH} CH_3CH_2OH \qquad (8)$$

RH: organics containing H in molecule.

At the high dose, the acetaldehyde-formation rate of Eq.5 is lower than the acetaldehyde-destroying rate of Eqs.(6)–(8). In other words, the acetaldehyde concentration decreases with increasing dose.

Figure 3 shows the ethanol concentration in aqueous DEHA solutions of 0.1–0.5 $mol{\cdot}L^{-1}$ irradiated to different doses. For DEHA samples of 0.1 and 0.2 $mol{\cdot}L^{-1}$ primary concentration, the ethanol content increases with the DEHA primary concentration, and its dependence on the absorbed dose is similar to that of acetaldehyde. For DEHA samples of primary concentration from 0.3 to 0.5 $mol{\cdot}L^{-1}$, however, the ethanol content decreases with the DEHA primary concentration, but increases all the way with the dose.

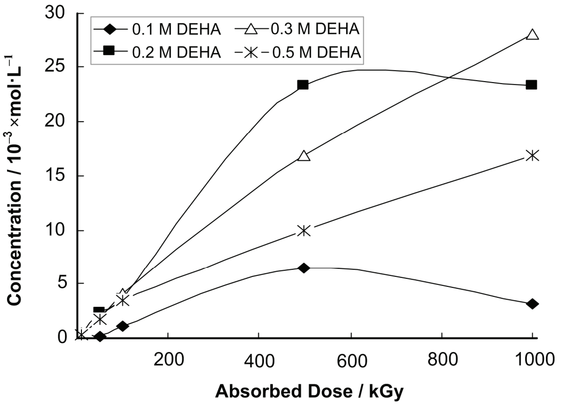

Fig.3 Ethanol concentration in aqueous DEHA solutions of 0.1–0.5 $mol{\cdot}L^{-1}$ irradiated to different doses.

At the low DEHA primary concentrations, ethanol was mainly produced by the reaction of acetaldehyde with e_{aq}^{-} and $H^{\cdot}$ (Eqs.(7) and (8)), hence its similar behavior to that of acetaldehyde. At the high DEHA primary concentrations, the γ-rays may react directly with DEHA and break the molecular bonds. The C-N bond is sensitive to radiation, it may be broken to form ethyl radicals.

$$(CH_3CH_2)_2NOH^{\cdot} \rightarrow \text{C-N break: } CH_2CH_3 \qquad (9)$$

The ethyl radical may react with $^{\cdot}OH$ to form ethanol:

$$CH_3\dot{C}H_2 + {}^{\cdot}OH \rightarrow CH_3CH_2OH \qquad (10)$$

An ethanol molecule, which has only single bonds, is less sensitive to radiation than an acetaldehyde and acetic acid molecule. This is the reason why the ethanol concentration always increases with the dose.

Figure 4 shows the concentration of acetic acid in aqueous DEHA solutions of 0.1–0.5 mol·L^{-1} irradiated to different doses. Although the concentration of acetic acid is low, it can be seen that its dose-dependence is similar to that of acetaldehyde, too, but it begins to decrease at a lower dose point.

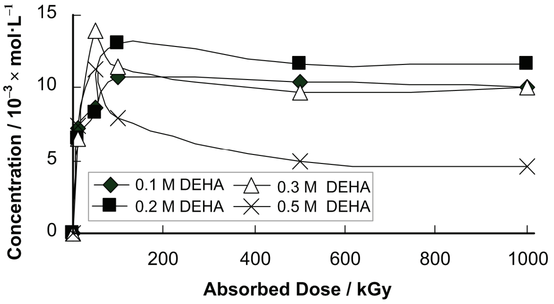

Fig.4 The concentration of acetic acid in aqueous DEHA solutions of 0.1–0.5 mol·L^{-1} irradiated to different doses.

The acetic acid was mainly produced by the reaction of acetaldehyde with ${}^{\cdot}OH$ (Eq.(6)), hence the similarity to acetaldehyde. On the other hand, the γ-rays may react directly with acetic acid at high dose, as given in Eq.(11).

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad (11)$$

The formation rate of acetic acid in Eq. (6) is lower than the destroying rate of acetic acid in Eq. (11), and the concentration of acetic acid decreases with increasing doses.

From Figs.2–4, the maximum concentrations of acetaldehyde, acetic acid and ethanol in the four irradiated DEHA samples (in primary concentration of 0.1, 0.2, 0.3, and 0.5 mol·L^{-1}) are 0.029, 0.014 and 0.028 mol·L^{-1}, respectively.

4 Conclusions

N,*N*-diethylhydroxylamine (DEHA) is a novel salt-free reducing agent used in the separation Pu and Np from U in the reprocessing of nuclear power spent fuel. This paper reports the study on the γ-radiolysis of DEHA in water and its radiolytic liquid organics. The radiolysis rate of DEHA increases with the absorbed dose, but decreases with primary DEHA concentration at 0.1–0.5 mol·L^{-1} irradiated to 10–1000 kGy. The main organic compounds produced by radiolysis of DEHA are acetaldehyde, ethanol and acetic acid. The concentration of acetaldehyde increases with the primary DEHA concentration, and it also increases with the absorbed dose at low dose, but decreases with the dose at high dose. The concentration of acetic acid is low, and the dependence of the concentration of acetic acid on the absorbed dose is similar to that of acetaldehyde. The relationship of ethanol concentration with the absorbed dose has something to do with the primary DEHA concentration. The maximum concentrations of acetaldehyde, acetic acid and ethanol are 0.029, 0.014 and 0.028 mol·L^{-1}, respectively.

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