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Gaseous products generated by radiation degradation of N,N-diethylhydroxylamine aqueous solution

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Abstract In this paper, gaseous products generated by radiation degradation of N,N-diethylhydroxylamine (DEHA) in aqueous solution are studied. The results show that by 10~1000 kGy irradiation of the solution in DEHA concentration of 0.1~0.5 mol·L^{-1}, the gaseous products were mainly hydrogen, methane, ethane and ethene. The volume fraction of hydrogen did not change much with different concentrations of DEHA. The volume fraction of methane and ethane decreased, but that of ethene increased, with increasing DEHA concentration. The volume fraction of hydrogen, methane and ethane increased with the dose. The relationship of the volume fraction of ethene with the dose had something to do with the DEHA concentration.

Key words N,N-diethylhydroxylamine, Radiation degradation, Gaseous product

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1 Introduction

In the use of nuclear fission reaction to generate energy, the spent nuclear fuel (SNF) has to be reprocessed to reclaim transuranium elements in many countries. Among the methods for SNF recovery, a popular choice is the PUREX process, by which U(VI) and Pu(IV) are co-extracted into organic phase from an aqueous nitric acid solution by tributylphosphate while other products retain in the aqueous phase, and Pu is subsequently separated from U(VI) by reducing Pu(IV) to Pu(III), which is stripped into the aqueous phase，with $Fe(NH_2SO_3)_2$ or U(IV)-$(NH_2)_2$. However, the use of Fe $(NH_2SO_3)_2$ increases the volume of radioactive wastes, and the use of hydrazine-stabilized U(IV) is not good, either, because dangerous hydrazoic acid can be produced by the reaction of hydrazine with nitrous acid. On the other hand, Np content in the SNF increases with burnup degree of the nuclear fuel[1] and, because Np valence cannot be controlled by Fe(II) or U(IV), the Np goes to different streams. Efforts have been made to overcome the drawbacks of the two reductants. Researchers[2-4] found that N,N-diethylhydroxylamine (DEHA) could quickly reduce Np(VI) and Pu(IV) to Np(V) and Pu(III), which were stable for certain period of time in acid solution. As an organic reductant, DEHA produces just alcohol, aldehyde, nitrogen/nitrogen oxide and other non-salt products, hence a salt-free reductant in future SNF treatment. In this paper, gaseous products generated by γ-ray degradation of aqueous DEHA solution are studied.

2 Experimental

2.1 Main equipment and accessories

A ^{60}Co irradiator of 3.6×10^{15} Bq at Shanghai Institute of Applied Physics, Chinese Academy of Sciences, a GC900A gas chromatograph and a 2 m ×3 mm packed 5 Å molsieve column from Shanghai Ke

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Chang Chromatograph Instruments Co. Ltd., and a 50 m ×0.53 mm capillary column with aluminum oxide from Lanzhou Institute of Chemistry and Physics, Chinese Academy of Sciences, were used in this study.

2.2 Standard gas mixture

Contents (in volume percentage) of the standard gas mixture, from Shanghai Institute of Measurement and Testing Technology, were H_2 (3.35), CO (0.097), CH_4 (1.052), C_2H_6 (0.954), C_2H_4 (0.099), C_3H_8 (0.049), C_3H_6 (0.046), *n*-C_4H_{10} (0.956), 1-C_4H_8 (0.053), *cis*-2-C_4H_8 (0.056), *trans*-2-C_4H_8 (0.053) and N_2 (93.235).

2.3 Sample preparation and irradiation

DEHA, supplied by China Institute of Atomic Energy, is in purity of 98.6%, as analyzed by gas chromatography. Aqueous DEHA solutions of 0.1, 0.2, 0.3 and 0.5 mol·L^{-1} were prepared with de-ionized water. Four milliliters of the solutions were placed into 7 mL penicillin bottles, which were sealed with a sealing machine and irradiated by ^{60}Co γ-rays to 10, 50, 100, 500 or 1000 kGy. The doses were monitored by dichromate dosimeters.

3 Results and discussion

3.1 Hydrogen produced by radiation degradation of DEHA

H_2 and CO gases evolved from irradiated aqueous DEHA solution were analyzed by gas chromatography with a thermal conductivity detector[5]. It was found that volume fraction of H_2 was very high, but that of CO was very low.

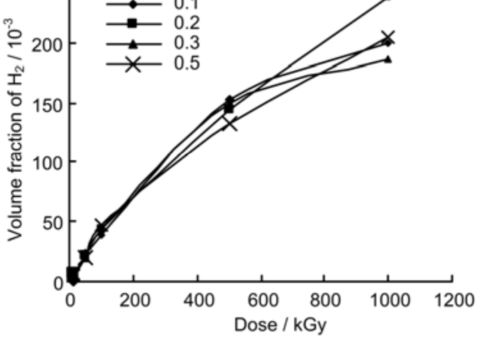

Fig.1 Volume fraction of H_2 in aqueous DEHA solutions of 0.1~ 0.5 mol·L-1 irradiated to different doses.

Fig.1 shows the H_2 generation at different doses. It can be seen that the H_2 volume fraction increases with the dose, but it does not change much with different concentrations of DEHA. When the dilute aqueous organic solution is irradiated, the chemical changes are mainly brought about by reactions between the active species from radiolysis of water and solute[6,7]. Under ionizing irradiation, as shown in Eq.(1), active species of H·, ·OH, e^-_{aq} and others are produced in the water of the DEHA solution.

$$H_2O \rightsquigarrow H\cdot, \cdot OH, e_{aq}, H_2, H_2O_2, H^+ \qquad (1)$$

The H· reacts with DEHA by hydrogen abstraction to give molecular hydrogen as follows:

$$H\cdot + (CH_3CH_2)_2NOH \rightarrow H_2 + (CH_3CH_2)_2NO\cdot \qquad (2)$$

The higher the dose is, the higher the H· concentration and the H_2 volume fraction are. But H· mainly comes from radiolysis of the water, which changes little in concentration when the DEHA concentration changes from 0.1 to 0.5 mol·L^{-1}. That is why the H_2 volume fraction does not change much at different concentrations of DEHA.

3.2 Light hydrocarbons produced by radiation degradation of DEHA

Light hydrocarbons released from radiation degradation of DEHA were analyzed with gas chromatography, with a 50 m ×0.53 mm capillary column coated with Al_2O_3 and a flame-ionization detector[8]. It was found that they were mainly methane, ethane and ethene. Volume fractions of the hydrocarbons at different doses are shown in Fig.2.

It can be seen from Fig.2a and 2b that the volume fraction of methane and ethane increases with the dose, but decrease with increasing concentration of DEHA at high doses. Methane and ethane may result from the breaking C-N and C-C bonds of the excited DEHA[9]:

$$(CH_3CH_2)_2NOH^* \rightsquigarrow \text{C - N break}: CH_3CH_2\cdot; \quad \text{C - C break}: CH_3\cdot \qquad (3)$$

Reactive $CH_3\cdot$ and $CH_3CH_2\cdot$ can react with DEHA by hydrogen abstraction to form CH_4 and C_2H_6:

$$CH_3\cdot + (C_2H_5)_2NOH \rightarrow CH_4 + (C_2H_5)_2NO\cdot \qquad (4)$$

$$CH_3CH_2\cdot + (C_2H_5)_2NOH \rightarrow CH_3CH_3 + (C_2H_5)_2NO\cdot \quad (5)$$

$CH_3\cdot$ can also react with $CH_3\cdot$ to form C_2H_6:

$$CH_3\cdot + CH_3\cdot \rightarrow CH_3CH_3 \quad (6)$$

Therefore, the concentrations of $CH_3\cdot$ and $CH_3CH_2\cdot$ produced by Eq.(3), and volume fractions of methane and ethane produced by Eqs.(4–6), increase with the dose.

In Fig.2c, the volume fraction of ethene increases with the DEHA concentration. For all the DEHA solutions, the volume fraction of ethene increases with the dose at low doses. At high doses, however, it decreases with increasing dose in low concentration DEHA solutions, but it changes little at high doses in high concentration DEHA solutions. Ethene may be produced as follows:

$$CH_3\cdot + CH_3CH_2\cdot \rightarrow CH_4 + CH_2 = CH_2 \quad (7)$$

$$CH_3CH_2\cdot + CH_3CH_2\cdot \rightarrow CH_3CH_3 + CH_2 = CH_2 \quad (8)$$

$$CH_3CH_2\cdot + (C_2H_5)_2NO\cdot \rightarrow (C_2H_5)_2NOH + CH_2 = CH_2 \quad (9)$$

The methyl and ethyl radicals increase with the dose, hence the increase of volume fractions of ethene. However, the Π bond of ethene is of low ionization potential, so the generated ethene can be removed via the following reaction:

$$CH_2 = CH_2 + Y\cdot \rightarrow \cdot CH_2CH_3Y \quad (10)$$

where Y· can be any radicals existing in the solution.

For low concentration DEHA solutions irradiated to high dose, the ethene-formation rate of Eqs.(7-9) is lower than the ethene-removing rate of Eq.(10), so the volume fraction of ethene decreases with increasing dose. But for high concentration of DEHA solutions irradiated to high doses, the ethene-formation rate can be equal to the ethene-removing rate, hence little change of the volume fraction of ethene in the high dose region.

The H_2 volume fraction in Fig.1 is much higher than the volume fractions of methane, ethane and ethene in Fig.2. This is simply because that the solutions contains far more amounts of water, from which H radicals are produced to form H_2, than DEHA, from which methyl and ethyl radicals are produced to form methane, ethane and ethene.

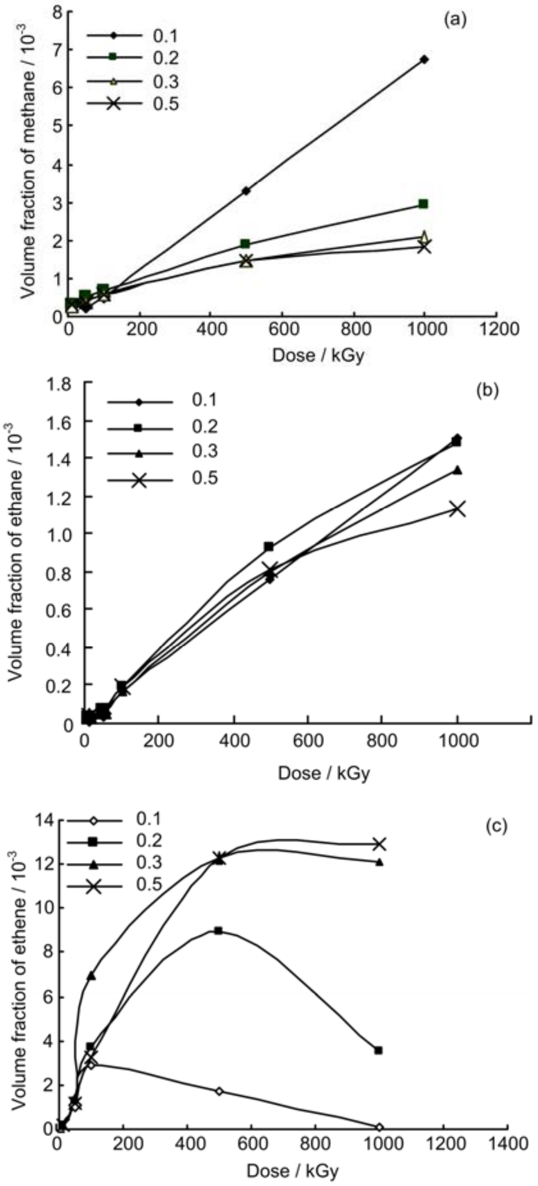

Fig.2 Volume fraction of methane (a), ethane (b) and ethene (c) in aqueous DEHA solutions of 0.1~0.5 mol·L^{-1} irradiated to different doses.

4 Conclusion

Gaseous products of radiation degradation of the reductant DEHA, used in reprocessing of power spent fuel, were studied. The results show that the gaseous products were mainly hydrogen, methane, ethane and ethene, and the volume fraction of hydrogen was much higher than that of methane, ethane and ethene. The volume fraction of hydrogen did not change much with different concentrations of DEHA. The volume fractions of methane and ethane decreased, but that of the ethene increased, with increasing concentration of DEHA. The volume fraction of hydrogen, methane and ethane increased with the dose. The relationship of the volume fraction of ethene with the dose had something to do with the concentration of DEHA.

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References

1 Ochsenfeld W, Petrich G. Sep Sci Technol, 1983, **18:** 1685-1698.

2 Sze Y K, Gosselin J A. Nucl Technol, 1983, **63:** 431-441.

3 Koltunov V S, Baranov S M, Zharova T P, *et al.* Radiokhimiya (in Russian), 1993, **35:** 79-84.

4 Zhang A Y, Hu J X, Zhang X Y, *et al.* Energy Sci Technol (in Chinese), 1999, **33:** 97-103.

5 Wang J H, Bao B R, Wu M H, *et al.* J Nucl Radiochem (in Chinese), 2004, **26:** 103-107.

6 Wu J L, Qi Sh Ch. Radiation chemistry (in Chinese). Beijing: Atomic Energy Publisher, 1993, 156-198.

7 Spinks J W T, Woods R J. An introduction to radiation chemistry, 2nd. New York: Wiley-Interscience Publication, John Wiley & Sons, 1976, 247-295.

8 Wang J H, Bao B R, Wu M H, *et al.* J Radioanal Nucl Chem, 2004, **262:** 451-453.

9 Cheng H Y, Xiang C L, Chen Y H. At Energy Sci Technol (in Chinese), 1964, **7:** 767-773.