Available online at www.sciencedirect.com
ScienceDirect
Nuclear Science and Techniques 19 (2008) 343–346
NUCLEAR SCIENCE AND TECHNIQUES

Analyses of organics in irradiated aqueous N, N-diethylhydroxylamine solution

WANG Jinhua[1,*] WAN Ying[1] WU Minghong[1] BAO Borong[1] SUN Xilian[1]
ZHENG Weifang[2] ZHANG Shengdong[2]

[1]*Shanghai Applied Radiation Institute, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 201800, China*

[2]*Radiochemistry Department, China Institute of Atomic Energy, Beijing 102413, China*

Abstract The organics in γ-ray irradiated aqueous N, N-diethylhydroxylamine (DEHA) solution, which is used as a reducing agent in reprocessing spent nuclear fuel, were analyzed with gas chromatography equipped with FFAP capillary column and flame-ionization detector. It was found that irradiated DEHA solutions contained acetaldehyde, ethanol, and acetic acid. For DEHA of 0.2 mol/L irradiated to 10~1000 kGy, the concents of acetaldehyde, ethanol and acetic acid are $(9.7\sim18.7)\times10^{-3}$, $(0.4\sim23.4)\times10^{-3}$ and $(6.5\sim11.7)\times10^{-3}$ mol/L, respectively. The concentration of DEHA decreases obviously with the dose.

Key words N, N-diethylhydroxylamine, Radiolysis, Organics analysis

CLC number O613.61

1 Introduction

The development of nuclear power industry is accompanied by increasing amount of spent nuclear fuel (SNF). To tackle the problem, many countries adopt a policy of closed nuclear fuel cycle for reprocessing SNF to isolate and recycle the residual uranium and plutonium, with PUREX (Plutonium-URanium EXtraction) being the most established process in the world. In this process, tributylphosphate (TBP) in kerosene is used to extract U (VI) and Pu (IV) from nitric acid solution, Pu is subsequently separated from U by reducing Pu (IV) to Pu (III), which is stripped into the aqueous phase, with ferrous sulfamate or U (IV)- hydrazine. The use of Fe^{2+}, however, introduces a lot of nonvolatile iron ions into the process, with increased volume of radioactive wastes to be stored, and the use of hydrazine produces explosive hydrazoic acid by the reaction of hydrazine with nitrous acid.

On the other hand, Np content increases with the burnup SNF[1], both Fe^{2+} and U (IV) cannot control Np valence, and this makes Np go to different streams. As an organic reducing agent, N,N-diethylhydroxylamine (DEHA) may be used as a salt-free reducing agent in PUREX process in future. It produces mainly alcohol, aldehyde, nitrogen, nitrogen oxide, etc. It can rapidly reduce Np (VI) and Pu (IV) to Np (V),and Pu (III) [2-4], which are slightly extractable by TBP from nitric acid solution. It can also stabilize Np (V) and Pu (III) in acid solution.

However, in the separation process, DEHA suffers from radiation decomposition, which may affect its reducing efficiency. The degradation product may also affect the partition of U, Pu and Np. In this paper, organics in γ-ray irradiated DEHA solution are analyzed.

2 Materials and methods

DEHA, in purity of 98.6%, was supplied by China Institute of Atomic Energy.

Supported by National Natural Science Foundation of China (20771074)

* Corresponding author. *E-mail address:* jinhuawang@staff.shu.edu.cn

Received date: 2008-04-23

The irradiation was done by ^{60}Co γ-rays in a source of 3.6×10^{15} Bq 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 (30m×0.25mm×0.25μm) was from Dalian Institute of Chemistry and Physics, Chinese Academy of Sciences.

DEHA of 0.2 mol/L was prepared with de-ionized water. Four millilitres of the solution was placed into a 7 mL penicillin bottle, which was sealed with rubber and aluminum and irradiated in the Co^{60} source to 10, 50, 100, 500 or 1000 kGy, monitored by dichromate dosimeters.

3 Results and discussion

3.1 Qualitative analysis of the organics

In aqueous DEHA solution irradiated by γ-rays, active species of H·, ·OH, e^-_{aq} and others are produced:

$$H_2O \rightarrow H\cdot,\ \cdot OH,\ e^-_{aq},\ H_2,\ H_2O_2,\ H^+ \quad (1)$$

H· or ·OH reacts with DEHA by H abstraction to give N, N-diethyl nitroxide radical:

$$H\cdot + (C_2H_5)_2NOH \rightarrow H_2 + (C_2H_5)_2NO \quad (2)$$

$$\cdot OH + (C_2H_5)_2NOH \rightarrow H_2O + (C_2H_5)_2NO\cdot \quad (3)$$

As there is air in the radiation system, O_2 in air can react with H·:

$$\cdot H + O_2 \rightarrow H_2O\cdot \quad (4)$$

And HO_2·can react with DEHA:

$$(C_2H_5)_2NOH + HOO\cdot \rightarrow (C_2H_5)_2NO\cdot + HOOH \quad (5)$$

N, N-diethyl nitroxide radical can self-react to form nitrone, which is hydrolyzed to form N- ethylhydroxylamine[5]:

$$2(C_2H_5)_2NO\cdot \longrightarrow CH_3CH{=}N(O)CH_2CH_3 + (C_2H_5)_2NOH \quad (6)$$

$$CH_3CH{=}N(O)CH_2CH_3 \xrightarrow[H^+]{H_2O} C_2H_5NHOH + CH_3CHO \quad (7)$$

Acetaldehyde may react with e^-_{aq} and H to form ethanol:

$$\cdot H + CH_3\overset{O}{\overset{\|}{C}}H \longrightarrow CH_3\overset{OH}{\overset{|}{C}}H\cdot \xrightarrow{RH} C_2H_5OH \quad (8)$$

$$e^-_{aq} + CH_3\overset{O}{\overset{\|}{C}}H \longrightarrow CH_3\overset{O^-}{\overset{|}{C}}H\cdot \xrightarrow{H_2O} CH_3\overset{OH}{\overset{|}{C}}H\cdot \xrightarrow{RH} C_2H_5OH \quad (9)$$

RH is organics containing H.

Acetaldehyde may react with oxidative species of HO_2· or ·OH to form acetic acid:

$$2CH_3CHO + 2HO_2\cdot \rightarrow 2CH_3COOH + H_2O_2 \quad (10)$$

$$CH_3CHO + \cdot OH \xrightarrow{\cdot R} CH_3COOH \quad (11)$$

R· is the radical in system.

On the other hand, DEHA reacts with ozone to form nitroethane[6], so organics in irradiated DEHA solution may be acetaldehyde, ethanol, acetic acid, nitroethane, N-ethylhydroxylamine and DEHA. The organics are of low boiling points: acetaldehyde (21°C), ethanol (78°C), acetic acid (118°C), nitroethane (114°C) and DEHA (128°C), and can be analyzed by gas chromatography.Gas chromatographic analyses of acetaldehyde, ethanol, acetic acid, nitroethane and DEHA were reported in Refs. [7]~[17], where most of the analyses were done with polar columns. The organics in this work are polar, too, and they should be analyzed by polar columns. FFAP and PEG20M are typical polar columns. Because the samples to be analyzed contain acetic acid and a lot of water, FFAP is better than PEG20M. As flame-ionization detector (FID) is very sensitive to organics, it was chosen in this study.

The column temperature was programmed so as to separate compositions in irradiated DEHA solution, and to reduce analysis time. The best analysis conditions were determined as initial column temperature of 60°C, initial isothermal period of 5 min, programmed heating rate of 6°C/min, final temperature of 100°C, final isothermal period of 5 min, and FID temperature of 150°C. Gas chromatograms of the standard organic mixture and the irradiated DEHA solution are shown in Fig. 1.

Comparing retention time of the peaks in Fig.1, one found that the sample contained no nitroethane but DEHA, acetaldehyde, ethanol and acetic acid. These were confirmed by adding the organics into the irradiated DEHA solutions and observing growth of corresponding peaks, which increased obviously.

By Eqs.(1)~(11), the organics in irradiated DEHA solutions can be acetaldehyde, ethanol, acetic acid,

nitroethane, N-ethylhydroxylamine and DEHA. As Fig.1b shows no nitroethane, the unknown peak at 12.49 min may be N-ethylhydroxylamine. In addition, a solution of HNO_3-0.2 mol/L DEHA was irradiated by γ-rays, but no peak at 12.49 min was observed in the gas chromatogram, indicating that that peak is N-ethylhydroxylamine, which was oxidized by HNO_3.

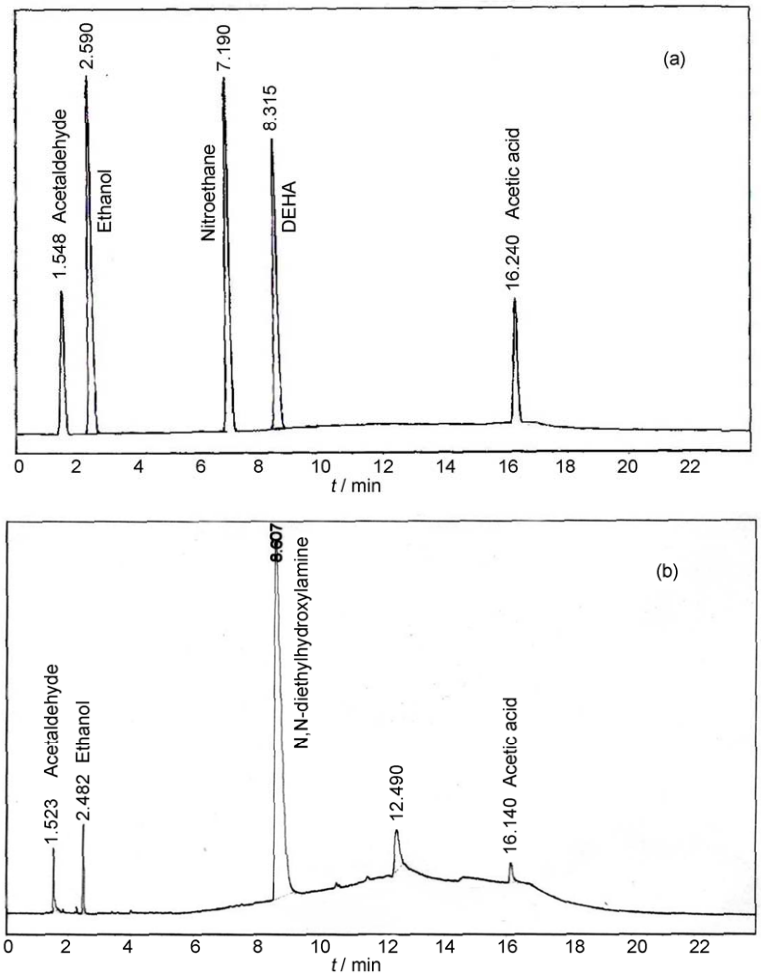

Fig.1 Gas chromatograms of (a) the standard organics mixture and (b) the irradiated DEHA solution.

3.2 Quantitative analysis of the organics

An external standard was used to perform quantitative analysis of the organics in irradiated DEHA solutions. Fittings results of the data are (with *r* being the correlation coefficient):

Acetaldehyde, $Y = -16.8+285528.3X$, r=0.9989;

Ethanol, $Y = 135.9 +1099370\ X$, r=0.9997;

Acetic, $Y = -1755.3 + 545544.8\ X$, r=0.9957;

DEHA, $Y = -8082.9 + 1874760\ X$, r=0.9997.

Peak areas of the organics in irradiated 0.2 mol/L DEHA solution are given in Table 1, from which the component concentration can be calculated by the formula above (Fig.2).

Table 1 Peak areas of the organics in irradiated 0.2 mol/L DEHA (μV·s)

Dose /kGy	CH_3CHO	CH_3CH_2OH	CH_3COOH	DEHA
10	2759.7	554.9	1767.2	304725.1
50	3352	2809.1	2751.4	291952.1
100	3554.4	4134.4	5395	285385.8
500	5330.7	25861.8	4624.5	175796.9
1000	4347	25760.9	4594.4	74871.4

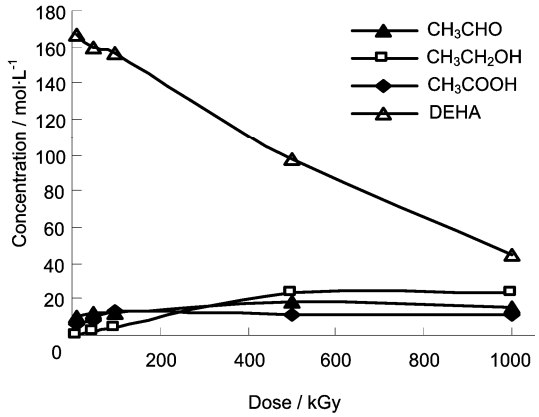

Fig.2 The organic contents in 0.2 mol/L DEHA solution irradiated to different doses.

From Fig.2, the ethanol concentration is higher than the acetaldehyde concentration, which is higher than that of acetic acid at higher doses. At lower doses, all organic concentrations increase with the dose, but the concentration changes are not obvious at higher doses. The DEHA concentration decreases markedly with the dose. The radiolysis rate of DEHA, i.e. difference of the initial and residual DEHA concentrations over initial DEHA concentration, is 22% at 100 kGy, and 50% at 500 kGy.

4 Conclusion

The qualitative and quantitative analyses of the organics in irradiated aqueous DEHA solution were performed. Results show that there are acetaldehyde, ethanol, acetic acid and DEHA in the solution. For DEHA of 0.2 mol/L irradiated to 10~1000 kGy, the acetaldehyde, ethanol and acetic acid concentrations are $(9.7\sim18.7)\times10^{-3}$, $(0.4\sim23.4)\times10^{-3}$ and $(6.5\sim11.7)\times10^{-3}$ mol/L, respectively. The concentration of DEHA decreases obviously with the dose.

References

1 Ochsenfeld W, Petrich G. Separation 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. Radiokhimiya, 1993, **35**:79-84.

4 ZHANG Anyun, HU Jingxin, ZHANG Xianye, *et al*. At Energy Sci Technol (in Chinese), 1999, **33**: 97-103.

5 Adamic K, Bowman D F, Gillan T, *et al*. J Am Chem Soc, 1971, **93** (4): 902-908.

6 Olszyna K, Heicklen J. Sci Total Environ, 1976, **5**:223-230.

7 WENG Banghua. Oil Nat Gas Chem Ind (in Chinese), 2001, **30**(6): 313-314, 320.

8 HAN Xiuli, LIU Jindun, MA Xiaojian. Liquor-making Sci Technol (in Chinese), 2007, **3**:103-104.

9 FEI Maoqing, GUO Lingyan. J Guangdong Public Secur (in Chinese), 2003, **1**: 8-9.

10 ZHANG Sufen, XIN Changbo, WANG Xi. Ind Water Treat (in Chinese), 2000, **20** (10): 27-30.

11 REN Qing, GUO Youjia. Chin J Chromatogr (in Chinese), 1997, **15**(4): 356-357.

12 HONG Wei, LÜ Qingsheng, TAN Manzhi, *et al*. J Jilin Univ (Engineering and Technology Edition), 2006, **36** (6):885-888.

13 WANG Huaming, CHENG Jiyuan. Chin J Synth Chem (in Chinese), 1997, **5**(1): 14-16.

14 WANG Xiaoning, CHEN Guanwei. Jiangsu Chem Ind (in Chinese), 1997, **25**(8):44-45.

15 JIAO Yuying. Environ Chem (in Chinese), 1985, **4**(1): 13-19.

16 LI Zhongbi. Synth Rubber Ind (in Chinese), 1992, **15**(4): 244-245.

17 China standard for chemical industry HG 2031-91(in Chinese).