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Radiolysis Products of Nitrate–Acetate Aqueous Solutions and Their Influence on pH of the Solutions

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Abstract—The influence of the components of nitrate–acetate aqueous solution and products of their radiolysis on pH of the solutions was experimentally studied in a wide dose range. The results can be used to estimate the speciation and migration conditions of radionuclides in a reservoir bed of underground disposed sites of liquid radioactive waste.

Here were continue our previous study [1] on radiochemical behavior of nitrate–acetate solutions used in deep disposal of nuclear waste [2]. In this study we examined experimentally the behavior of the radiolysis products of nitrate–acetate solutions and their influence of pH of aqueous solutions with the aim to estimate the speciation and migration conditions of radionuclides in a reservoir bed.

The composition of the radiolysis products of aqueous acetic acid solutions was studied insufficiently [2, 3]. The data on radiolysis of aqueous nitrate solutions were reviewed in the monograph [3]. However, the behavior of radiolysis products of acetates in aqueous nitrate solutions exposed to prolonged irradiation has not been studied quantitatively.

EXPERIMENTAL

We studied aqueous solutions simulating the macrocomposition of radioactive waste and containing 0.125 M nitric acid, 0.24 M acetic acid, and 1.17 M sodium nitrate. The pH of nonirradiated model CH_3COOH–$NaNO_3$, $NaNO_2$–CH_3COOH–$NaNO_3$, and $NaNO_2$–$NaNO_3$ solutions was measured. The composition of the model solutions was similar to that of irradiated solutions.

The kinetic curves of decomposition of nitric and acetic acids on exposure to γ-ray radiation of ^{60}Co and accumulation of their radiolysis products were studied in a temperature-controlled glass cell at 23°C and a dose rate of 1.2 Gy s^{-1}.

The content of nitric and acetic acids and of liquid acidic radiolysis products of acetic acid in the samples was determined by potentiometric titration, with the determination error not exceeding 10%. The concentration of sodium nitrite was determined by the calorimetric procedure described in [4]. The pH was measured with an Ekotest-2000 pH meter.

RESULTS AND DISCUSSION

The potentiometric titration procedure used allowed determination of the concentration of nitric acid and the total concentration of acetic acid (HAc) and its acidic radiolysis products. The dependences of the concentrations of HNO_3, acidic organic compounds (HAc + products), and $NaNO_2$ in the solutions containing 0.125 M HNO_3, 0.245 M HAc, and 1.2 M $NaNO_3$ and of pH of these solutions on the radiation dose are presented in Table 1 and Fig. 1.

Table 1. Concentration of components (M) and pH of nitrate–acetate solutions at different radiation doses

Dose, MGy	HAc + products	HNO_3	$NaNO_2$	pH
0	0.245	0.125	0	0.7
0.21	0.210	0.065	–	0.95
0.39	0.180	0.030	–	1.75
0.6	0.147	0.025	–	2.35
1.0	0.105	0	–	2.70
1.6	0.068	0	–	3.15
2.0	0.065	0	0.017 (0.027)*	2.8 (4.5)*
2.4	0.075	0	0.024 (0.038)*	3.0
2.8	0.03	0	0.034 (0.051)*	3.75 (5.5)*
3.6	0.006	0	0.060 (0.100)	4.05 (6.2)*

* Ten days after irradiation.

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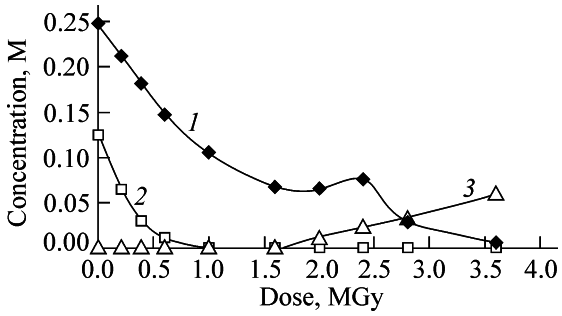

Fig. 1. Concentration of (*1*) HAc + radiolysis products, (*2*) HNO_3, and (*3*) $NaNO_2$ as a function of radiation dose.

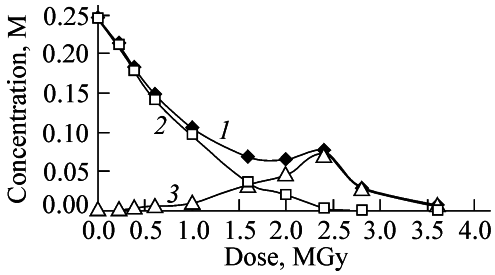

Fig. 2. Concentration of (*1*) HAc + radiolysis products, (*2*) HAc, and (*3*) radiolysis products as a function of radiation dose.

The initial radiation-chemical yield of HNO_3 decomposition (1.4 molecule/100 eV) was consistent with our previous results [1]. Radiolysis of 0.125 M HNO_3 solution is complete at doses lower than 1 MGy. Nitrous acid was not detected up to complete decomposition of HNO_3. Probably, in acid solution, HNO_2 is completely spent for oxidation of CH_3COOH to form nitrogen dioxide. In the absence of HNO_3, $NaNO_2$ is accumulated with the radiation-chemical yield of 0.26 molecule/100 eV. The low yield of nitrite ions is due to their oxidation with hydrogen peroxide.

Table 2. Experimental and calculated concentrations (M) of CH_3COOH and its radiolysis products in nitrate–acetate solutions at different radiation doses

Dose, MGy	HAc + products, experiment	HAc, calculation	Products, calculation
0	0.245	0.245	0
0.21	0.210	0.210	0
0.39	0.180	0.177	0.003
0.6	0.147	0.141	0.006
1.0	0.105	0.096	0.009
1.6	0.068	0.035	0.033
2.0	0.065	0.020	0.045
2.4	0.075	0.003	0.072
2.8	0.03	0	0.03
3.6	0.006	0	0.006

The yield of HAc radiolysis was determined at low radiation doses (up to 0.2 MGy) when the influence of the acidic radiolysis products was minimal. The yield is 1.2 and 0.8–0.9 molecule/100 eV in the presence and in the absence of HNO_3, respectively, which agrees with our previous data [1]. The HAc consumption and the total accumulation of its radiolysis products were calculated in the whole range of radiation doses at a constant yield of HAc radiolysis. The results are presented in Table 2 and Fig. 2.

The experimental dependences of the concentrations of HAc and its acidic radiolysis products on the radiation dose (Fig. 2, curve *1*) can be accounted for on the basis of our calculations. The maximum at 1.5–3 MGy is due to accumulation of acidic radiolysis products which are more stable to radiolysis than HAc. The total radiation-chemical yield of decomposition of the acidic radiolysis products can be estimated from the data of Table 2 and the portion of curve *1* (Fig. 2) in the range of radiation dose from 2.4 to 3.6 MGy where the HAc concentration is close to zero. The total radiation-chemical yield of decomposition of acidic products (0.55 molecule/100 eV) is lower by a factor of 1.5 than the yield of decomposition of HAc (0.8 molecule/100 eV) in the absence of HNO_3. The acidic products are accumulated in a radiation-chemical yield of 0.34 molecule/100 eV in the dose range 1–2.4 MGy in the absence of HNO_3. Since the increase in the product concentration is proportional to the difference between the yield of their formation and decomposition, the total yield of the product formation should be equal to 0.34 + 0.55 = 0.89 molecule/100 eV, which is close to the initial yield of HAc decomposition under these conditions.

The main final liquid products of radiolysis of nitrate–acetate solutions are glyoxylic acid ($CHO\cdot COOH$), glycolic acid ($CH_2OHCOOH$), succinic acid $(CH_2COOH)_2$, formaldehyde (CH_2O), and sodium nitrite [3, 4]. Formation of these compounds can be tentatively described by the following general scheme:

$$H_2O \xrightarrow{\gamma} H,\ OH,\ e^-_{aq},\ H_2O_2,\ H_2; \quad (1)$$

$$CH_3COOH + H(OH) \rightarrow CH_2COOH + H_2(H_2O); \quad (2)$$

$$CH_2COOH + O_2 \rightarrow O_2CH_2COOH; \quad (3)$$

$$2O_2CH_2COOH \rightarrow CH_2(OH)COOH + CH(O)COOH + O_2; \quad (4)$$

$$2CH_2COOH \rightarrow (CH_2COOH)_2; \quad (5)$$

$$NO_3^- + e_{aq}^- \rightarrow NO_3^{2-} + H_2O \rightarrow NO_2 + 2OH^-; \quad (6)$$

$$NO_3^- + H \rightarrow HNO_3^- \rightarrow NO_2 + OH^-; \quad (7)$$

$$NO_2 + NO_2 \rightarrow N_2O_4; \quad (8)$$

$$N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+; \quad (9)$$

$$H_2O_2 + NO_2^- \rightarrow NO_3^- + H_2O. \quad (10)$$

The products are formed mainly by reaction of acetic acid with radical products of water radiolysis [reactions (1), (2)]. In the presence of HNO_3, HAc additionally decomposes by the reaction with nitrogen dioxide:

$$CH_3COOH + NO_2 \rightarrow CH_2COOH + HNO_2. \quad (11)$$

In the presence of dissolved oxygen, acetate radicals form the peroxy radicals [reaction (3)] which disproportionate [reaction (4)] to form glycolic and glyoxylic acids. These reactions compete with recombination of acetate radicals (5) to form succinic acid. The recombination yield increases with a decrease in the oxygen content in the irradiated solution.

This reaction scheme is not complete and requires an experimental study to estimate the kinetic parameters of accumulation and consumption of the radiolysis products.

The pH of the irradiated solutions is determined by a change in the concentrations of the initial components and their radiolysis products. At the radiation dose of up to 1 MGy, the pH of solutions is determined mainly by the HNO_3 concentration. It increases from 0.7 to 2.7 as the HNO_3 concentration decreases from the initial value to 0. The pH of aqueous solutions of acetic acid with the concentration equal to that in the irradiated solutions is 2.7. When the radiation dose is higher than 1 MGy, the pH depends on the concentration ratio of HAc, its acidic radiolysis products, and $NaNO_2$. Sodium nitrite increases the pH of the solutions, and acidic radiolysis products of HAc decrease the pH. Comparison of pH of the irradiated solutions with that of model aqueous $NaNO_3$ solutions containing the same amounts of HAc and $NaNO_2$ (Fig. 3) confirms this conclusion.

The results presented in Fig. 3 and Table 1 allow the following conclusions.

When HNO_3 is present in an irradiated solution (0.5–1 MGy), the pH is determined by its concentration.

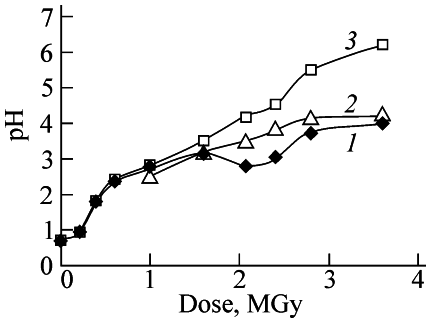

Fig. 3. The pH of (*1*) the solutions right after irradiation, (*2*) the model nonirradiated HAc + sodium nitrite solution, and (*3*) the solution 15 days after the irradiation, as a function of the radiation dose.

In the dose range from 1 to 2 MGy (in the absence of HNO_3), the pH is determined by the concentrations of HAc and $NaNO_2$; the influence of acidic radiolysis products of HAc on the pH in this dose range is negligible.

In the dose range from 2 to 4 MGy, the pH (on the background of low HAc concentration) depends on the concentration ratio of acidic radiolysis products of HAc and $NaNO_2$. The acidic products decrease pH to a greater extent than does HAc, and $NaNO_2$ increases it. The minimum on the pH–dose curve (Fig. 3) appears at the concentration ratio of these products formed at the radiation dose from 2 to 3 MGy.

The pH of model HAc + $NaNO_2$ + $NaNO_3$ solutions (Fig. 3, curve *2*) is similar to that of the irradiated solutions of the similar composition (Fig. 3, curve *1*). The only exception is solutions irradiated to doses of 2–3 MGy. In this case the pH is lower owing to the maximal concentrations of acidic radiolysis products of HAc.

The following postradiation effects are observed. During storage of the irradiated solutions, their pH increases (Fig. 3, curve *3*) as well as the $NaNO_2$ concentration in these solutions (Table 1). This is probably due to slow (at room temperature) chemical reduction of nitrate ions with radiolysis products of HAc.

The quantitative relationships of the behavior of the initial components and radiolysis products of nitrate–acetate solutions should be taken into account in long-term prediction calculations of the state of filtered acidic liquid radioactive waste in deep disposal sites. To calculate the dose rate and residence time of wastes in a bed, data on the average activity

of the waste are required. To calculate the radius of their distribution in the bed, the total volume of wastes disposed of within this time should be known.

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