RADIOLYSIS OF NITRATE-ALCOHOL BINARY MIXTURES AT pH 12

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Gamma-radiolysis of alkaline binary mixtures of nitrate-alcohol (1-propanol and 1-butanol) has been investigated at a fixed pH of 12. The products of radiolysis, mainly nitrite, aldehyde and hydrogen peroxide were estimated. Also the effect of concentration of each species present in the mixture on the G-values of the products formed has been examined. The G-values of each of the products are found to be lower in basic medium in binary mixtures as compared to those obtained at neutral pH; other conditions being kept constant. However, the yields of products in nitrate solutions show higher values at basic pH in comparison with their counterparts at neutral pH. Results are explained on the basis of reaction mechanism that operates during the process of radiolysis, leading to the formation of the different products.

Introduction

Several reports are available in the literature1-10 which account for the radiolysis of neutral aqueous solutions in presence of different types of solutes, N_2O, O_2, NO_3, IO_4, S_2O_3^2-, etc., normally being used as e_{aq} and H atom scavengers, while organic solutes like acetates, formates and alcohols as scavengers for hydroxyl radicals. However, no reports are available on the radiolysis of binary mixtures containing two different types of solute in alkaline solutions except for two reports11,12 on the radiolysis of alkaline solutions containing nitrate ions.

In the present work we have carried out studies on the radiolysis of nitrate ions and binary mixtures containing alcohol (1-propanol and 1-butanol) in basic medium at 12 pH. Further, the effect of concentration of each species in the mixture by varying one and keeping the other constant and vice versa has also been explored. The yields of the products are observed to differ from those obtained at neutral pH. These are explained by accounting for the difference in the reaction mechanism involved during radiolysis at 7 and 12 pH.
Experimental

A. R. grade chemicals were used in the experiments. Aqueous solutions were prepared by using doubly distilled water. Binary mixtures of nitrate and alcohol (1-propanol and 1-butanol) were prepared by mixing suitable quantities of each solute so as to obtain the required concentration. Alkaline pH 12 was obtained by using sodium hydroxide. The pH of the solution was measured using a pH meter. The solutions were irradiated in a 7.4 TBq 60Co gamma-source supplied by BARC, Bombay, India, with a dose rate of 1.7 kGy h⁻¹. Samples were kept in stoppered tubes during irradiation.

After irradiation the samples were neutralized by using hydrochloric acid and then analyzed for nitrite, aldehyde and hydrogen peroxide formed as the stable products.

Nitrite was estimated by using the modified SHINN's method. In this a diazo complex is formed on addition of acidic sulfanilamide and 1-naphthylethylenediamine dihydrochloride. The absorbance of the pink colored complex was measured at λ\text{max} of 540 nm with 52 000 mol⁻¹ · cm² as the extinction coefficient.

JOHNSON and SCHOLES method was used to find the amount of aldehyde formed in the sample. In this, the aldehyde was first converted into 2,4-di-nitrophenylhydrazone derivative and extracted in carbon tetrachloride in 2–3 fractions. It gives a reddish brown complex on addition of ethanolic sodium hydroxide, which absorbs at λ\text{max} of 430 nm. The concentration was determined by using molar extinction coefficient value of 18 800 mol⁻¹ · cm².

Hydrogen peroxide was estimated by GHORMLEY's method. Hydrogen peroxide reacts with potassium iodide in the presence of molybdenum catalyst and undergoes rapid oxidation to form tri-iodide ion. Absorbance of this ion was measured at λ\text{max} of 350 nm the extinction coefficient being assumed to be 2336 mol⁻¹ · cm².

Results

Figure 1 shows the yield of nitrite formed as a function of dose absorbed in alkaline solutions at various concentrations. The G-values of nitrite calculated from the slopes of the linear plots are given in Table 1. The corresponding G(NO₂⁻) values obtained at neutral pH reported earlier are also included in Table 1.

From the values in Table 1 it is observed that the G-values increase with increasing concentration of nitrate. But when we compare the G-values at pH 7 and pH 12, the yields at pH 12 are found to be higher at all concentrations studied. Also the G-value does not show saturation in basic medium as against the one observed in the neutral medium.