SPECIATION OF Pu IONS BY DIFFERENTIAL PULSE POLAROGRAPHY

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By means of differential pulse polarography, Pu ions of different oxidation states have been investigated in 1M Na₂CO₃ solution. Redox reactions of Pu/III/, Pu/IV/, Pu/V/ and Pu/VI/, which are mostly of irreversible nature, have been observed within the potential range of the dropping mercury electrode /DME/, from 0 to -1.5 V, against a Ag/AgCl/NaCl(3M) reference electrode. Based on the peak potential observed for each reaction, the stability of a given oxidation state in the solution could be ascertained. The redox potential of the Pu/IV/-Pu/III/ pair, which was found to be -1.0 V, indicated that the Pu/IV/ carbonate complex was of high stability. The detection sensitivity of the Pu/IV/ ion was found to be 1x10⁻⁶M.

INTRODUCTION

With growing interest in the chemical behaviour of actinide ions in groundwater, the carbonate complexation of these ions has been recently attracting particular
attention, because of the ubiquitous presence of carbonate ions in groundwater and their pronounced tendency to complex with heavy metal ions\textsuperscript{1-3}. Electrochemical properties of plutonium in carbonate solutions can provide information about its probable redox reactions in groundwater. In the past, only a few works have been devoted to the electrochemical investigation of Pu ions in carbonate solutions\textsuperscript{3-7}. As a part of speciation study of Pu ions we determined the oxidation and reduction potentials of different redox pairs of Pu ions in carbonate solutions by differential pulse polarography, which facilitates measuring of irreversible electrode processes\textsuperscript{8}, as expected in this system, with high sensitivity.

EXPERIMENTAL

Polarograms are measured with a Polarecord E 506 /Metrohm Co./ using the three-electrode technique. Sample solution of 20 ml is introduced in a temperature-controlled reaction cell /25 + 0.2 °C/, which consists of a dropping mercury electrode /DME/, a secondary working electrode alternatively of platinum net or of mercury pool, a Ag/AgCl/NaCl(3M) reference electrode, a platinum foil auxiliary electrode, and a pH electrode. The reference and auxiliary electrodes are separated from the experimental solution by a ceramic diaphragm. Measurements are carried out under Ar atmosphere in the potential range from 0 to -1.5 V against the reference electrode with a potential scan rate of 15 mV/s and a pulse height of -50 mV. The drop time of DME is adjusted at 0.4 s.

With a $^{239}$Pu starting solution /0.012% $^{238}$Pu, 90.24% $^{239}$Pu, 9.33% $^{240}$Pu, 0.42% $^{241}$Pu/ in 1M HClO$_4$, the Pu ions of different oxidation states are prepared electrochemical-