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ELECTROLYTIC BEHAVIOR OF ACETYLACETONE AT LEAD DIOXIDE ELECTRODE IN AQUEOUS SOLUTION

Taitiro FUJINAGA and Tadayosi YOSHIMURA*

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

**Department of Industrial Chemistry, Fukui Technical College, Sabae-shi, Fukui 916*

By using electro-deposited lead dioxide (PbO_2) electrode as an indicator, the electrode reaction of acetylacetone in aqueous solution was investigated. In conclusion, it was found that in the cathodic process electrode lead dioxide is reduced to lead ion which reacts with acetylacetone to form the complex and in the anodic process the lead complex is oxidized again and deposited onto the electrode as lead dioxide.

Acetylacetone is a polar aprotic solvent slightly miscible with water, and has been widely used as an extraction solvent and also as a chelating agent in the spectrophotometric determination of various metal ions[1,2]. Fujinaga et al.[1,3] have recently reported on the polarographic determination of uranium(VI) and iron (III) using acetylacetone as a chelating agent, an extracting solvent, and an electrolysis medium. However, the oxidation behavior of acetylacetone has not yet been investigated. Lead dioxide has been employed as an oxidizing agent, an electrode substance[4], and a working electrode of electrometric titration[5,6]. Presently, using the electro-deposited PbO_2 electrode as an indicator electrode, the electrolytic behavior of acetylacetone in aqueous solutions was investigated.

The β-lead dioxide (PbO_2) electrode was prepared by the electrolytic oxidation of lead nitrate on a platinum microelectrode ($0.102\ cm^2$)[4]. All voltammetric measurements were carried out at 25°±0.2°C without deaeration of solution. A saturated calomel electrode (SCE) was used as a reference electrode.

Cyclic current-voltage curves for $0.1\ mol\ dm^{-3}$ KNO_3 solution at the PbO_2 electrode did not show any anodic or cathodic wave when sweeping at $30\ mV\,s^{-1}$ in the region of the potential sweep, +0.5 ∿ +1.5 V vs.SCE (see Figure 1-a). In Figure 1-b and c, the anodic peak at +1.00 V and the cathodic peak at +0.80 V due to acetylacetone were first obtained. The heights of two peaks increased with the increase of the acetylacetone concentration. The anodic peak corresponds to the reoxidation of lead complex to form lead dioxide, and the cathodic peak corresponds to the reduction of lead dioxide in the presence of acetylacetone; in the cathodic process electrode lead dioxide is reduced to lead ion which reacts with acetylacetone to form the complex and in the anodic process the lead complex is oxidized again and deposited onto the electrode as lead dioxide, according to the following reaction scheme:

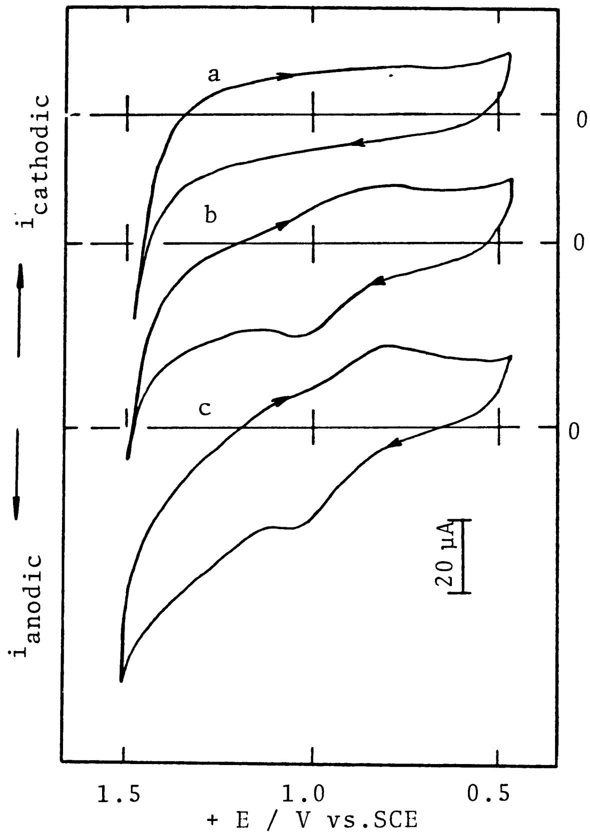

Figure 1 Cyclic current-voltage curves of acetylacetone at PbO_2 electrode in 0.1 mol dm^{-3} KNO_3 solution(pH 5.0), and the sweep rate, 30 mV s^{-1}. Concn. acetylacetone: curves a,0; b,2.0; c,5.0 mmol dm^{-3}.

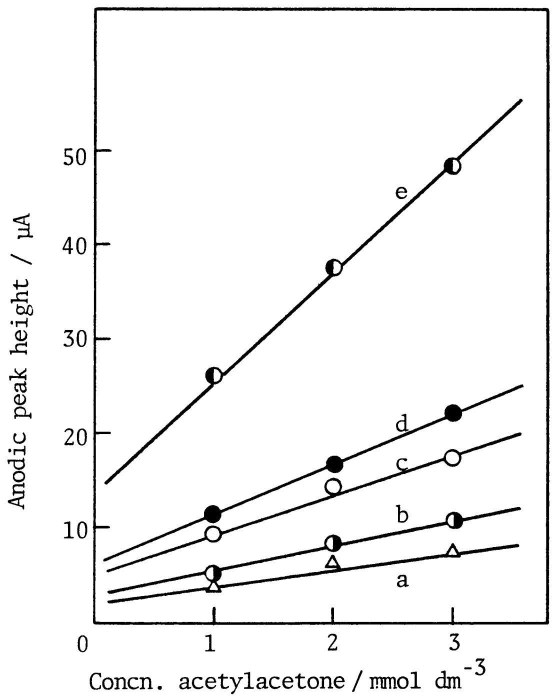

Figure 2 Relationship between anodic peak height and concn. of acetylacetone at PbO_2 electrode in 0.1 mol dm^{-3} KNO_3(pH 5.0). Sweep rate: lines a,3.3; b,10; c,30; d,33.3; e,100 mV s^{-1}.

$$PbO_2 + 2\,HAA + 2\,H^+ + 2\,e^- \rightleftharpoons PbAA_2 + 2\,H_2O$$

where HAA and $PbAA_2$ denote acetylacetone and lead acetylacetonate, respectively.

The effect of acetylacetone concentration on the height of anodic and cathodic peaks at PbO_2 electrode was investigated. As shown in Figure 2, the height of the peaks is directly proportional to the acetylacetone concentration. By the measurement of anodic peak height with the PbO_2 electrode, it is possible to determine acetylacetone of the concentration down to 1×10^{-3} mol dm^{-3}. Therefore, the PbO_2 electrode seems to be useful for determining a chelating agent such as acetylacetone.

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