TECHNICAL REPORT

POLAROGRAPHIC DETERMINATION OF XANTHATES

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Xanthates give well-defined anodic waves in the presence of pyridine and some other auxiliary electrolyte. The diffusion current obtaind is proportional to the concentration of xanthate and the calibration curve can be utilized for its quantitative determination.

Xanthates are widely used in the manufacture of rayon and also as mineral collectors in the froth flotation process of concentrating low grade ores. Potassium ethyl xanthate has been widely used as extracting agent[1] for the determination of various metal ions. A new solvent system[2] has been introduced in the extraction technique for metal xanthates. This reagent has also been used in the amperometric determination[3] of some metal ions. A potentiometric and polarographic method has also been reported by Cap and others[4] which was later modified by Sun and Holzmann[5].

In the present study the polarographic behaviour of potassium ethyl and butyl xanthates in different supporting electrolytes containing potassium chloride or sodium nitrate and 0.2M pyridine has been investigated in detail. The study of these xanthates at the D.M.E. reveal that the product of the anodic reaction is strongly adsorbed at the mercury drop as indicated by a prewave.

EXPERIMENTAL

Xanthates are prepared from distilled alcohols, potassium hydroxide (B.D.H. analar grade) and carbon disulphide, and are recrystallised. The supporting electrolytes are prepared from B.D.H. chemicals. Pyridine (B.D.H.) is used. 0.01% gelatin is used in the case of butyl xanthate. Demineralised water is used throughout the work.

Polarograms are recorded at 25± 0.5°C, with Adept polarograph. D.M.E. and S.C.E. connected to the cell through potassium chloride agar bridge are used as electrodes. Double distilled mercury is used and the capillary characteristics m and t are 2.733mg./sec. and 3.1 sec. respectively in distilled water and open circuit. Nitrogen is passed to remove the dissolved oxygen.

Stock solutions of Xanthates (0.05M) are prepared and different aliquotes of these solutions are used with the supporting electrolytes.

CHARACTERISTICS OF THE ANODIC WAVES

The effect of the variation of pyridine concentration has been studied. The diffusion current is constant upto 0.5M but is suppressed when the concentration of pyridine is increased beyond 1.2M. The $E_{\frac{1}{2}}$ is constant in the range 0.2M to 0.6M while it shifted to more negative side as the concentration of pyridine is increased. There is very little effect when the concentration of potassium chloride or sodium nitrate is between 0.1M and 0.5M. The effect of temperature has been studied from 15° to -50°C and the value of the temperature coefficient is found to be 1.6 -1.8%/degree C.

Polarograms of 4.0×10^{-3} M butyl xanthate at different heights of mercury column have been obtained and the plot of i_d vs h is a straight line indicating the diffusion-controlled nature of the oxidation.

Relation between the diffusion current and xanthate concentration

The plot of diffusion current vs concentration of xanthate is a straight line in the concentration range 1.5×10^{-3} to 7.0×10^{-3}. Above this concentration the behaviour becomes erratic. The diffusion current constant is found to be 1.54.

The plot of $\log \frac{i}{(i_d - i)}$ vs. E is a straight line having a slope of 0.0592. Applying the Lingane equation, the value of n corresponds to 1. Alternately the value of $E_{\frac{3}{4}-\frac{1}{4}}$ has been calculated and was found to be 62.5mV, indicating one-electron oxidation and the formation of RSHg is, therefore, inferred according to the equation

$$RSH + Hg \rightarrow RSHg + H^+ + e^-$$

An adsorption wave was observed with concentration 0.3×10^{-3} xanthate solution. It reached a constant value at xanthate concentration equal to or larger than 1.2×10^{-3}M.

RESULTS AND DISCUSSIONS

At pH 7.0, the current–voltage curves at the D.M.E. of xanthate in presence of 0.2M pyridine and the other electrolyte (potassium chloride or sodium nitrate) have the same appearance.

All polarograms exhibit the characteristic prewave at the negative of the main wave due to the strongly adsorbed film of RSHg (R = ethyl or butyl). This wave is obtained even in the presence of alcohol indicating that the alcohol do not displace the film responsible for this wave. As is typical with the adsorption wave, the height of the prewave increases upto a particular limit and remains constant after a particular concentration of xanthate.

The polarograms of xanthate show that anodic diffusion current is proportional to the concentration upto 6 mM xanthate with pyridine and in the presence of other electrolytes (potassium chloride or sodium nitrate) suggesting the use of these waves for the quantitative determination of the xanthates. The waves obtained are well defined and do not show any minimum as reported earlier, and the calibration curve is linear over a wide range.

The behaviour of butyl xanthate is quite similar to that of ethyl xanthate but for the fact that the half-wave potential shifted to –0.335V.

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