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EFFECT OF DISSOLVED OXYGEN ON OSCILLOGRAPHIC POLAROGRAMS

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A feature of oscillographic (cathode-ray) polarography is the possibility of applying it to fixed electrodes and to those having a slowly changing surface. This characteristic has been utilised by Gokhshtein[1,2] for analytical determination in the presence of dissolved air. The test solution was subjected to a preliminary electrolysis at a potential sufficiently negative to reduce the ion to be determined, an anodic pulse was then applied, and the dissolution current of the amalgam which had been formed was recorded. If the duration of the preliminary electrolysis (delay) is sufficiently great, considerable depletion of oxygen in the layer adjacent to the electrode occurs under these conditions, and there is practically no interference by dissolved oxygen with the analytical determination[1,2].

On the other hand, several papers on oscillographic polarography have noted that dissolved oxygen gives no reduction wave even in the absence of preliminary electrolysis, and the occurrence of this reduction on the electrode surface can be assessed only from the effect of reduction products of O_2 on other processes occurring at the same time (for example, formation of cadmium hydroxide during reduction of Cd^{2+}).[3-7] This phenomenon has not been adequately explained and, in conjunction with the work cited[1,2], might have given rise to the belief that oscillographic polarography offers the possibility of analytical determinations in the presence of dissolved oxygen.

Examination of published results[3-7] shows that a common feature of this work is the use of oscillographic polarographs employing alternating current or voltage (for example, a sinusoidal current in ref.3, a polycyclic sawtooth voltage in ref.4, a polycyclic triangular voltage in refs.5-7). The results obtained in refs.3-7 can therefore be explained as follows.

When periodic pulses of any form are applied to an electrode, the boundary conditions for the start of each successive pulse change until a limit is reached, when the so-called cyclic state[8] ensues, which is recorded by the instrument. Under these conditions the sensitivity to strongly irreversible processes is only about 5% of that to reversible processes[9,10]. A qualitative explanation of this result is that, with a strongly irreversible reaction, the substance used up during each negative pulse is not balanced during the period of anodic voltage, whereas complete or partial compensation does occur in the case of a reversible process. As a result, the surface concentration of the reactant becomes considerably lower with irreversible than with reversible reactions.

The concentration of O_2 in water at 25° is 0.25×10^{-3} M,[6] and it is still less in 1 M KCl. Since the reduction of O_2 is strongly irreversible, the maximum current for each stage in the reduction of O_2,

$$O_2 + 2H_2O + 2e = H_2O_2 + 2OH^- \text{ and } H_2O_2 + 2e = 2OH^-,$$

when periodic pulses are used, will not exceed the faradaic current of the reversibly reducible ions (Cd^{2+}) present at a concentration 10^{-5} M. In other words, the oxygen current under these conditions is considerably smaller than the charging current (as was stated in refs.3-7), and can be neglected.

When, however, an oscillographic polarograph with a single sawtooth voltage pulse[11-13] is used, the maximum current is of the same order of magnitude for reversible and irreversible processes, with $\alpha n_a = 1$, $n = 2$, $(I_M)_{irr} = 0.8(I_M)_{rev}$.[14a] In this case, therefore, waves for both stages in the reduction of O_2 may be expected to appear in a solution of an inert electrolyte (KCl), and also O_2 may be expected to affect the oscillographic polarograms for the reduction of various ions. Experiments which we have carried out with a TsLA oscillographic polarograph[12], using 1 M KCl solutions containing different amounts of $CdCl_2$, confirm this conclusion (Fig.1).

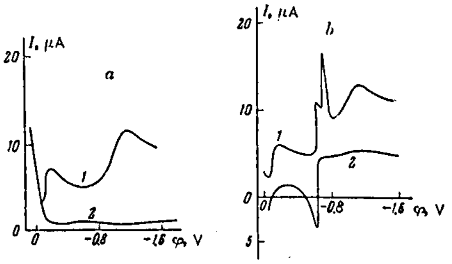

Fig.1. Oscillographic polarograms at a dropping mercury electrode with $v = 1.0$ V sec^{-1}, $t_{prelim} = 1.4$ sec, $m = 1.6$ mg × × sec^{-1}, $\varphi_{init} = 0.0$ V, and $\varphi_{fin} = -1.6$ V (relative to mercury on bottom of cell):
a) cathodic oscillograms in 1*N* KCl: 1) in the presence of O_2; 2) after removal of O_2;
b) in 1*N* KCl + 4×10^{-4} *N* $CdCl_2$ in the presence of O_2; 1) cathodic oscillogram; 2) anodic oscillogram.

Fig. 1*b* shows that the reduction currents for Cd^{2+} and $Cd(OH)_2$ are superimposed on that for O_2 and H_2O_2 on the cathodic oscillogram. When the anodic oscillogram is being obtained, the anodic current for the dissolution of cadmium amalgam is subtracted, after a certain delay (1.4 sec), from the cathodic current for the reduction of O_2. The effect of dissolved oxygen is rather smaller in the latter case, since the surface concentration of O_2 decreases somewhat during the delay. In this case too, however, the oxygen current is very large, which makes it impossible to increase the sensitivity of the instrument, and consequently does not allow small quantities of Cd^{2+} ($< \sim 10^{-5}$ M) to be determined†. It follows from Fig. 2, in conformity with refs. 5 and 6, that the height of the cathodic peaks for the reduction of Cd^{2+} and $Cd(OH)_2$ is not a linear function of the concentration of cadmium salt. This suggests that the currents due to cadmium and to oxygen are combined in a non-additive way. Nevertheless, the height of the peak for the anodic dissolution of cadmium amalgam is linearly related to the $CdCl_2$ concentration, and the magnitudes of the anodic currents can be employed for the analytical determination of cadmium in the presence of dissolved air.

It follows from the above that in general the conclusion that dissolved oxygen has no effect in the analysis of solutions by oscillographic polarography requires certain qualifications. Indeed, in the case of oscillographic polarograms obtained with polycyclic sawtooth scanning dissolved oxygen apparently does not interfere with the analytical determination[4], but the sensitivity of the method is limited by the quite large capacitive current[10]. The sensitivity of oscillographic polarography can be increased by using a single scan with a low rate of change of the voltage[14b], but in the case of a dropping electrode having a normal drop time (3–5 sec) this advantage disappears in the presence of dissolved oxygen owing to the strong distortion of the oscillograms by the relatively large oxygen reduction current. Thus oscillographic polarography can be employed to determine small concentrations (10^{-5} M) of ions in the presence of dissolved air only if fixed electrodes or electrodes with a low drop rate ($t > 10$ sec), an anodic voltage, and a comparatively long period of preliminary electrolysis[1,2] are used.

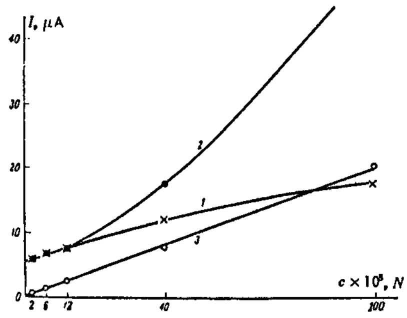

Fig. 2. Dependence of the maximum current on the concentration of $CdCl_2$ in 1 N KCl in the presence of O_2 (v = 1.0 V sec^{-1}; m = 1.6 mg sec^{-1}; t_{prelim} = 1.4 sec): 1) cathodic current due to the reduction of Cd^{2+}; 2) cathodic current due to the reduction of $Cd(OH)_2$; 3) anodic current due to the oxidation of cadmium amalgam.

We wish to express our gratitute to Academician A. N. Frumkin for looking through the manuscript and discussing the experimental results.

SUMMARY

The conditions have been examined under which dissolved oxygen has no effect on oscillographic polarograms, and an explanation is given for this phenomenon. The general conclusion that dissolved oxygen has no effect on oscillographic polarograms requires qualification.

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† As already mentioned, considerably better results can be achieved by using fixed or slowly dropping electrodes and by increasing the period of delay (preliminary electrolysis) before application of the anodic pulse,[1,2] since under these conditions the layer adjacent to the electrode is very greatly depleted in O_2.

INTERNAL STRESSES ARISING DURING CATHODIC OCCLUSION OF HYDROGEN BY METALS

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The occlusion of hydrogen by metals often produces internal stresses in the latter, which may be large. These stresses have sometimes been regarded as the main cause of both the decrease in strength and the appearance of