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Effect of Acetic acid on the Polarographic Behavior of Copper(II) Acetate in Acetonitrile

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Dimeric copper(II) acetate in acetonitrile solution is reduced at the dropping mercury electrode and gives a two-step reduction wave. The reduction wave is distorted in dilute $LiClO_4$ and $NaClO_4$ solutions.[1] This distortion results from the interaction of alkali metal ions with acetate ions which are liberated from the monovalent copper species.

Acetic acid in acetonitrile solution keeps the liberated acetate ions from precipitating as an insoluble film of alkali metal acetates on the surface of the electrode. The present investigation deals with the polarographic behavior of copper(II) acetate in acetonitrile in the presence of acetic acid.

The experimental details were the same as previously described.[2,3]

Results and Discussion

The effect of acetic acid on the polarograms of copper(II) acetate in $NaClO_4$ solution is shown in Fig. 1. With small amounts of acetic acid present,

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[1] E. Itabashi, *J. Electroanal. Chem.*, **36**, 179 (1972).

[2] E. Itabashi and S. Ikeda, This Bulletin, **42**, 1901 (1969).

[3] E. Itabashi and S. Ikeda, *J. Electroanal. Chem.*, **26**, 97 (1970).

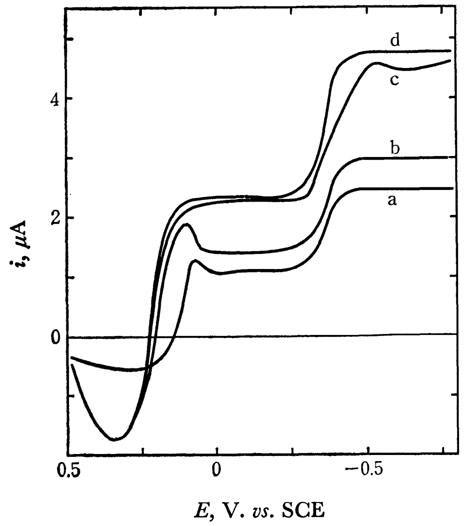

Fig. 1. Effect of the acetic acid concentration on the polarograms of 0.5 mM copper(II) acetate in 0.05M NaClO$_4$. [CH$_3$COOH]: (a), 0; (b), 0.032%; (c), 0.064%; (d), 0.096%.

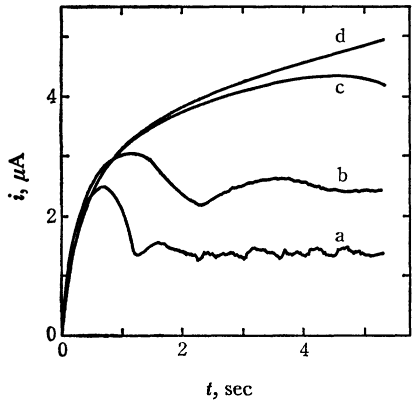

Fig. 2. Effect of the acetic acid concentration on the *i-t* curves for the reduction wave of 0.5 mM copper(II) acetate in 0.05M NaClO$_4$. The electrode potential is set up at −0.55 V *vs.* SCE. [CH$_3$COOH]: (a), 0; (b), 0.032%; (c), 0.064%; (d), 0.096%.

the limiting current of the wave was enhanced, and a peak current was observed in the anodic part. When the concentration of acetic acid exceeded 0.1% in volume, there was no apparent change in the shape of the developed wave. The zero current potential is a mixed potential where the cathodic current caused by the one-electron reduction of copper(II) acetate to monovalent copper species is equal to the anodic current caused by the oxidation of mercury to mercuric acetate. In the absence of acetic acid, the current-time (*i-t*) curves of individual drops at the constant potential exhibited remarkable irregularities at the whole potential region examined. Figure 2 presents the typical *i-t* curves in NaClO$_4$ solution in the presence and the absence of acetic acid. This irregularity is due to the formation of the insoluble film of sodium acetate on the surface of the electrode. On addition of small amounts of acetic acid, the irregularities of the *i-t* curves disappeared when the acetic acid concentration reached a critical value. The *i-t* curves for the reduction wave in 0.05M NaClO$_4$ solution containing 0.1% acetic acid had the characteristics of normal diffusion control. This result suggests that acetic acid keeps the liberated acetate ions from precipitating as an insoluble film of sodium acetate on the electrode surface. The solubility of sodium acetate in NaClO$_4$ acetonitrile solution was found to increase as the acetic acid concentration increased.

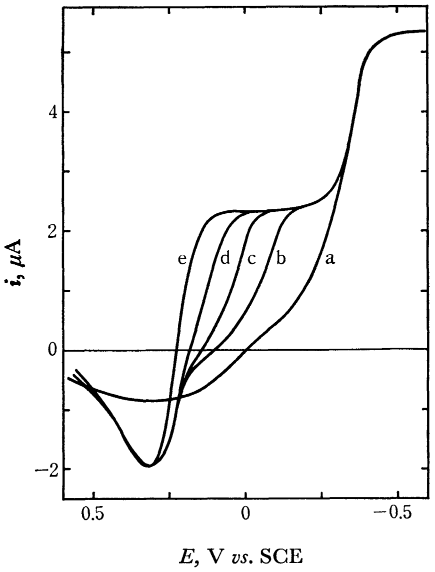

Fig. 3. Effect of the acetic acid concentration on the polarograms of 0.5 mM copper(II) acetate in 0.05M *n*-Bu$_4$NClO$_4$. [CH$_3$COOH]: (a), 0; (b), 0.032%; (c), 0.096%; (d), 0.24%; (e), 0.64%.

In the presence of acetic acid, the one-electron reduction wave of copper(II) acetate to monovalent copper species shifts towards more positive potentials. This is due to the shift of the potential of mercury dissolution and not to the involvement of any chemical reaction prior to the electron transfer of copper(II), because there was no apparent change on the absorption spectrum of copper(II) acetate in acetonitrile with and without acetic acid. A similar displacement of the one-electron reduction wave was also observed in tetra-*n*-buthylammonium perchlorate (*n*-Bu$_4$NClO$_4$) solution in the presence of acetic acid, as shown in Fig. 3. In *n*-Bu$_4$NClO$_4$ solution in the absence of acetic acid, no well-defined one-electron reduction wave was observed. The value of the limiting current at −0.65 V *vs.* SCE corresponds to a two-electron reduction, that is, Cu(II)→Cu(O). With acetic acid present, the one-electron reduction wave began to appear and shifted towards more positive potentials as the acetic acid concentration increased. The half-wave potentials of the anodic wave caused by the oxidation of mercury to mercuric acetate in 1.0 mM *n*-Bu$_4$NOAc and 0.05M *n*-Bu$_4$NClO$_4$ solutions in the presence and the absence of 0.64% acetic acid were found to be +0.24 V and −0.02 V *vs.* SCE, respectively. Therefore, the appearance of the one-electron reduction wave of Cu(II) to Cu(I) results from the displacement of the anodic wave caused by the oxidation of mercury to mercuric acetate.

The anodic part of the composite anodic-cathodic waves in the presence of acetic acid exhibits a peak current rather than a limiting plateau. This peaking could be the result of the difference in the electron numbers involved in the anodic and cathodic prosesses. It was predicted by Vlček[4] that the anodic part of the composite wave exhibits a peak current when the electron number involved in the anodic process caused by the electrooxidation of the reduction products is larger than that in the cathodic process. The reaction mechanism of the composite anodic-cathodic waves of copper(II) acetate at the dropping mercury electrode may be written as follows.

$$1/2Cu_2(OAc)_4 + e \longrightarrow 1/2Cu_2(OAc)_4{}^{2-} \quad (1)$$

$$1/2Cu_2(OAc)_4{}^{2-} \xrightarrow{k} Cu(I) + 2OAc^- \quad (2)$$

$$2OAc^- + Hg \longrightarrow Hg(OAc)_2 + 2e \quad (3)$$

where the coordinated molecules were omitted for convenience, and k is the rate constant for the dissociation reaction of monovalent copper species. The peak current of the anodic part has the characteristics of kinetically control. The exponent of the i-t curves for the peak current of the anodic wave in 0.05 M n-Bu_4NClO_4 solution containing acetic acid had a value of 0.52±0.02. This value is well beyond the value of 0.17 expected for a diffusion controlled electrode mechanism. This could indicate that the rate of the reaction (2) is finite in order that the limiting current is attained.

The author would like to express his hearty thanks to Professor Shigero Ikeda.

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[4] A. A. Vlček, "Progress in Inorganic Chemistry," Vol. 5, ed. by F. A. Cotton, Interscience Publishers, New York, N. Y. (1963), p. 321.