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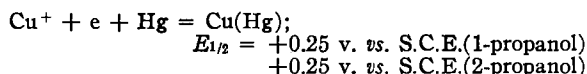
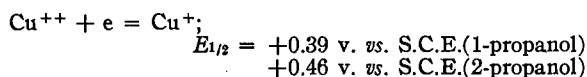
## Polarographic Evaluation of the Copper(II), Copper(I) and Copper(I), Copper Potentials in Ethanol and Methanol

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Received July 24, 1961

The effect of complex formation between Cu(I) ion and allyl alcohol on the polarographic behavior of Cu(II) and Cu(I) ions in methanol and ethanol has been used to evaluate the formal potentials (polarographic half-wave potentials) for the Cu(II), Cu(I) and Cu(I), Cu(Hg) couples in these two alcohols. The following values (*vs.* S.C.E.) were obtained:  $E^{0'}_{\text{Cu(II), Cu(I)}} = +0.200$  v. and  $E^{0'}_{\text{Cu(I), Cu(Hg)}} = +0.145$  v. in methanol;  $E^{0'}_{\text{Cu(II), Cu(I)}} = +0.340$  v. and  $E^{0'}_{\text{Cu(I), Cu(Hg)}} = +0.235$  v. in ethanol. Through voltammetric studies with a rotating platinum electrode, the following values (*vs.* S.C.E.) for the potential of the Cu(I)(1 M), Cu couple were obtained:  $E_{\text{Cu(I), Cu}} = +0.135$  v. in methanol;  $E_{\text{Cu(I), Cu}} = +0.265$  v. in ethanol.

The electrochemical behavior of copper(II) ion in ethanol and methanol at the dropping mercury electrode is similar to that in water, *i.e.*, reduction to the metal proceeds in one step. The reduction potentials for copper(I) ion in ethanol and methanol therefore appear to be, as in water, more positive (easier for reduction) than those for the reduction of copper(II) ion to copper(I) ion. On the other hand, the electrochemical reduction of copper(II) ion in 1-propanol and 2-propanol proceeds reversibly in two steps, copper(II) to copper(I) and copper(I) to copper metal, with these potentials<sup>1</sup>



This striking difference in polarographic behavior of Cu(II) ion in the lower alcohols has prompted an investigation of the potentials of the copper couples in methanol and ethanol. Potentials for the copper couples in ethanol and methanol were obtained by studying the effect of complex formation between copper(I) and allyl alcohol on the polarographic behavior of copper(II) and copper(I) ions and by the use of the rotating platinum electrode. Allyl alcohol was chosen as the complexing agent because of its known ability to form a 1:1 complex with Cu(I) ion in water<sup>2</sup> and because Cu(II) ion is not one of a limited

group of transition metal ions which form olefin complexes.

### Experimental

Absolute methanol and absolute ethanol were treated with magnesium activated with iodine and fractionally distilled. Highest available purity allyl alcohol was dried with anhydrous potassium carbonate and fractionally distilled after filtration from the potassium carbonate. The methanol and ethanol polarographic solutions, 0.1 M in LiClO<sub>4</sub>, were *ca.* 10<sup>-3</sup> and 10<sup>-2</sup> M; respectively, in water. Water was determined by the Karl Fischer method. Anhydrous lithium perchlorate and copper(II) perchlorate hexahydrate (G. F. Smith Chemical Co.) were dried in a vacuum oven at 60° and used without any pretreatment. The "dried" copper(II) perchlorate salt was analyzed by electrolytic deposition of the copper. The value of 18.75% obtained for the copper content of the dried salt (theoretical for the anhydrous salt 24.21%) indicates that only two moles of water were removed in the drying operation. For polarographic studies, methanol solutions were *ca.* 2 × 10<sup>-4</sup> M in Cu(II), 1 × 10<sup>-1</sup> to 1 × 10<sup>-3</sup> M in allyl alcohol, and 0.1 M LiClO<sub>4</sub>. Ethanol solutions were *ca.* 5 × 10<sup>-4</sup> to 1 × 10<sup>-4</sup> M in Cu(II), 1 × 10<sup>-2</sup> to 5 × 10<sup>-4</sup> M in allyl alcohol, and 0.1 M in LiClO<sub>4</sub>. Stock methanol and ethanol solutions of allyl alcohol were used to adjust the concentration of allyl alcohol. The stock solutions were prepared by diluting measured volumes of allyl alcohol to known volumes with methanol and ethanol.

Polarograms were recorded with a Leeds and Northrup Type E Electrochemograph at 25°. An H-type cell was used; the dropping mercury electrode was placed in one side arm and a slowly flowing aqueous saturated calomel electrode in the other. A slow flow of potassium chloride solution from the electrode was necessary to prevent formation of a crust of salt on the tip of the electrode which caused the resistance of the cell to change during a polarographic scan. Solutions were deoxygenated with purified nitrogen. Polarograms were corrected for the *iR* drop across the cell. An Industrial Instrument Co. Conductivity Bridge Model RC 16B2 was used to make the resistance measurements.

(1) I. V. Nelson, R. C. Larson, and R. T. Iwamoto, *J. Inorg. & Nuclear Chem.*, in press.

(2) R. M. Keefer, L. J. Andrews, and R. E. Kepner, *J. Am. Chem. Soc.*, **71**, 3906 (1949).

## Results and Discussion

In methanol and ethanol in the presence of allyl alcohol, Cu(II) is reduced in two steps at the dropping mercury electrode. Stepwise reduction of Cu(II) occurs because Cu(I) is stabilized through complex formation by allyl alcohol, and Cu(II) either does not form a complex with allyl alcohol or forms a weaker complex than Cu(I). If the electrode reactions are reversible, the expressions

$$E_{d.e. Cu(II), Cu(I)} = E^0_{Cu^{++}, Cu^+} + 0.059 \log \frac{C^0_{Cu^{++}} f_{Cu^{++}}}{C^0_{Cu^+} f_{Cu^+}} \quad (1)$$

and

$$E_{d.e. Cu(I), Cu(Hg)} = E^0_{Cu^+, Cu(Hg)} + 0.059 \log \frac{C^0_{Cu^+} f_{Cu^+} a_{Hg}}{C^0_{Cu(Hg)} f_{Cu(Hg)}} \quad (2)$$

in which  $C^0$  is the molar concentration at the surface of the mercury drop,  $a_{Hg}$  is the activity of mercury at the surface of the drop, and  $f_{Cu^{++}}$ ,  $f_{Cu^+}$ , and  $f_{Cu(Hg)}$  are the activity coefficients of  $Cu^{++}$  ion,  $Cu^+$  ion, and copper amalgam, respectively, give the potential of the dropping mercury electrode at any point on the polarographic wave.<sup>3</sup> If we assume that Cu(II) ion does not form a complex with allyl alcohol, A, use  $S$  to denote the sum of uncomplexed and complexed,  $CuA(1:1 \text{ complex})$ ,  $Cu(I)$  species

$$S = C_{Cu^+} + C_{CuA} \quad (3)$$

and

$$K_{inst.} = \frac{C_{Cu^+} f_{Cu^+} C_A f_A}{C_{CuA} f_{CuA}} \quad (4)$$

the potential of the dropping mercury electrode at any point on the waves as a function of the concentration of allyl alcohol,  $C_A$ , is given by the expressions

$$E_{d.e. Cu(II), Cu(I)} = E^0_{Cu^{++}, Cu^+} + 0.059 \log \frac{(K_{inst.} + C_A f_A) C^0_{Cu^{++}} f_{Cu^{++}}}{K_{inst.} S f_S} \quad (5)$$

$$E_{d.e. Cu(I), Cu(Hg)} = E^0_{Cu^+, Cu(Hg)} + 0.059 \log \frac{K_{inst.} S f_S a_{Hg}}{(K_{inst.} + C_A f_A) C^0_{Cu(Hg)} f_{Cu(Hg)}} \quad (6)$$

in which  $f_A$  and  $f_S$  are the activity coefficients of allyl alcohol and  $S f_S$  would be essentially  $f_{CuA}$  if  $CuA$  is a strong complex. Incorporating the standard relationships between polarographic current and surface concentration of the potential governing species into equations 5 and 6 and fol-

lowing the usual treatment,<sup>3</sup> we obtain

$$E_{d.e. Cu(II), Cu(I)} = E^0_{Cu(II), Cu(I)} + 0.059 \log \frac{K^*_{inst.} + C_A}{K_{inst.}} + 0.059 \log \frac{i_d - i}{i} \quad (7)$$

and

$$E_{d.e. Cu(I), Cu(Hg)} = E^0_{Cu(I), Cu(Hg)} + 0.059 \log \frac{K_{inst.}}{K^*_{inst.} + C_A} + 0.059 \log \frac{i_d - i}{i} \quad (8)$$

where

$$E^0_{Cu(II), Cu(I)} = E^0_{Cu^{++}, Cu^+} + 0.059 \log \frac{f_A k_S f_{Cu^{++}}}{f_S k_{Cu^{++}}} \quad (9)$$

and

$$E^0_{Cu(I), Cu(Hg)} = E^0_{Cu^+, Cu(Hg)} + 0.059 \log \frac{f_S k_{Cu(Hg)} a_{Hg}}{f_{Cu(Hg)} f_A k_S} \quad (10)$$

$k_{Cu^{++}}$ ,  $k_{Cu(Hg)}$ , and  $k_S$  are the proportionality constants relating polarographic current to the concentrations of  $Cu^{++}$ , and  $Cu(Hg)$  and  $S$  at the electrode surface.  $i$  and  $i_d$  in equations 7 and 8 are the polarographic current at any point on the wave and the diffusion current, respectively. Also in equations 7 and 8  $K^*_{inst.}$  is  $K_{inst.}/f_A$ .

Equations 1-10 were tested by analysis of the polarograms. The average values of  $\Delta E_{d.e.}/\Delta \log (i_d - i)/i$  shown for the polarographic waves indicate that the waves are reversible and the basic equations above can be used to describe the current voltage curves.<sup>3</sup>

	$\Delta E_{d.e.}/\Delta \log \frac{i_d - i}{i}$
Methanol	
Cu(II), Cu(I) wave;	0.062 v.
Cu(I), Cu(Hg) wave;	0.063 v.
Ethanol	
Cu(II), Cu(I) wave;	0.063 v.
Cu(I), Cu(Hg) wave;	0.065 v.

The half-wave potentials for the two steps in the polarograms are given by

$$E_{1/2 Cu(II), Cu(I)} = E^0_{Cu(II), Cu(I)} + 0.059 \log \frac{K^*_{inst.} + C_A}{K_{inst.}} \quad (11)$$

$$E_{1/2 Cu(I), Cu(Hg)} = E^0_{Cu(I), Cu(Hg)} + 0.059 \log \frac{K_{inst.}}{K_{inst.} + C_A} \quad (12)$$

which simplify when  $S$  is essentially equal to  $C_{CuA}$  to the more familiar expressions

$$E_{1/2 Cu(II), Cu(I)} = E^0_{Cu(II), Cu(I)} + 0.059 \log \frac{1}{K_{inst.}} + 0.059 \log C_A \quad (13)$$

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., Chapter XII.

TABLE I  
 EVALUATION OF  $E^0_{\text{Cu(II),Cu(I)}}$  AND  $E^0_{\text{Cu(I),Cu(Hg)}}$ 

$C_{\text{allyl alc.}} \times 10^2$	$E_{1/2\text{Cu(II),Cu(I)}}^{c,d}$ vs. S.C.E.	$E_{1/2\text{Cu(I),Cu(Hg)}}^{c,d}$ vs. S.C.E.	$pK^*_{\text{inst. Cu(I),allyl alc.}} f$	$E^0_{\text{Cu(II),Cu(I)}}$ vs. S.C.E.	$E^0_{\text{Cu(I),Cu(Hg)}}$ vs. S.C.E.
Methanol <sup>a</sup>					
11.7	0.310 v.	0.025 v.		0.188 v.	0.145 v.
1.17	.265 v.	.080 v.	3.0 ± 0.1	.200 v.	.145 v.
0.88	.260 v.	.085 v.		.202 v.	.144 v.
.59	.255 v.	.095 v.		.206 v.	.144 v.
.294	.225 v.	.110 v.		.190 v.	.145 v.
.117	.220 v.	.125 v.		.200 v.	.145 v.
				Av. 0.200 v. <sup>d</sup>	0.145 v. <sup>d</sup>
Ethanol <sup>b</sup>					
1.18	0.425 v.	0.150 v.		0.338 v.	0.237 v.
0.330	.400 v.	.180 v.	3.4 ± 0.2	.344 v.	.236 v.
.236	.390 v.	.185 v.		.341 v.	.234 v.
.141	.370 v.	.195 v.		.332 v.	.233 v.
.094	.370 v.	.210 v.		.341 v.	.239 v.
.047	.350 v.	.220 v.		.332 v.	.238 v.
				Av. 0.340 v. <sup>d</sup>	0.235 v. <sup>d</sup>

<sup>a</sup> *ca.*  $2 \times 10^{-4}$  M in  $\text{Cu}^{++}$ . <sup>b</sup> *ca.*  $1 \times 10^{-4}$  to  $5 \times 10^{-4}$  M in  $\text{Cu}^{++}$ . <sup>c</sup> Uncertainty of  $E_{1/2}$  values is 0.005 v. <sup>d</sup> These values have been rounded to the nearest 0.005 v. Uncertainty of  $E^0$  values is *ca.* 0.010 v. \*  $\text{LiClO}_4$  supporting electrolyte.  $f K^*_{\text{inst.}} = \frac{K_{\text{inst.}}}{f_{\text{allyl. alc.}}} \cong K_{\text{inst.}}$

$$E_{1/2\text{Cu(I),Cu(Hg)}} = E^0_{\text{Cu(I),Cu(Hg)}} + 0.059 \log K_{\text{inst.}} + 0.059 \log \frac{1}{C_A} \quad (14)$$

The slopes of 0.95 and 1.02 for the plots of  $E_{1/2\text{Cu(I),Cu(Hg)}}$  vs.  $-0.059 \log C_A$  indicate that in methanol and ethanol in the concentration ranges of Cu(I) ion and allyl alcohol investigated, Cu(I) ion forms a 1:1 complex with allyl alcohol. The values of 0.90 and 0.97 for the slopes of the plots of  $E_{1/2\text{Cu(II),Cu(I)}}$  vs.  $0.059 \log C_A$  indicate that in methanol and ethanol Cu(II) ion does not form a complex with allyl alcohol. If Cu(II) ion did form a 1:1 complex in the concentration ranges of Cu(II) ion and allyl alcohol used in this study, the half-wave potential for the Cu(II),Cu(I) wave would be constant and independent of the concentration of allyl alcohol. If the Cu(II) complex involved more than one allyl alcohol, the slope of  $E_{1/2\text{Cu(II),Cu(I)}}$  vs.  $0.059 \log C_A$  would be  $-1$ ,  $-2$ , etc.

In order to obtain the values of  $E^0$ , we find that  $K_{\text{inst.}}$  has to be evaluated first. From equation 12 it follows that the shift of the half-wave potential of the Cu(I),Cu(Hg) couple with changing concentration of allyl alcohol should obey the expression<sup>4</sup>

$$E_{1/2(2)} - E_{1/2(1)} = 0.059 \log \frac{K^*_{\text{inst.}} + C_{A(1)}}{K^*_{\text{inst.}} + C_{A(2)}} \quad (15)$$

(4) (a) A similar expression with the log term inverted can be obtained from equation 11; (b)  $K^*_{\text{inst.}}$  is evaluated by calculating first an approximate  $K^*_{\text{inst.}}$  using the total concentration of allyl alcohol,  $C_A$ . The approximate  $K^*_{\text{inst.}}$ 's are used to correct the values of  $C_A$  for the amount of allyl alcohol tied up by Cu(I) ion.

The  $K^*_{\text{inst.}}$  values obtained through equation 15 are listed in Table I as  $pK^*_{\text{inst.}}$ . The rather large uncertainty in the  $pK^*_{\text{inst.}}$  values is due to the small differences in  $E_{1/2}$  values. The  $pK^*_{\text{inst.}}$  values obtained, 3.0 in methanol and 3.4 in ethanol, are in reasonable agreement with the value of 4.8 for  $pK_{\text{inst.}}$  reported by Keefer, Andrews, and Kepner<sup>2</sup> for complex formation in water.

$E^0$  values were obtained from equations 11 and 12 by using the corrected values of  $C_A$  and  $K^*_{\text{inst.}}$  in place of  $K_{\text{inst.}}$ . The validity of the approximation  $K^*_{\text{inst.}} = K_{\text{inst.}}$  is considered in the latter part of this section. Values for  $E^0$  are listed in Table I.

The potentials (vs. S.C.E.) of the copper couples,  $E^0_{\text{Cu(II),Cu(I)}} = +0.200$  v. and  $E^0_{\text{Cu(I),Cu(Hg)}} = +0.145$  v. in methanol and  $E^0_{\text{Cu(II),Cu(I)}} = +0.340$  v. and  $E^0_{\text{Cu(I),Cu(Hg)}} = +0.235$  v. in ethanol, are not in the reverse order as they are in water, in which the solvation energy of Cu(II) ion is very high. The one-step polarograms of Cu(II) ion in methanol and ethanol, therefore, are not due to similar situations as in water but to the closeness of  $E^0_{\text{Cu(II),Cu(I)}}$  and  $E^0_{\text{Cu(I),Cu(Hg)}}$  to each other. Interestingly, the slopes of the reduction waves of Cu(II) ion in methanol and ethanol, 0.042 and 0.064, respectively, also reflect this situation.

The  $E^0$  values indicate that the solvating properties of methanol and ethanol for copper ions are

more like those of 1-propanol and 2-propanol than water.

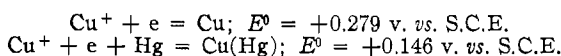
The values of  $E^{0'}_{\text{Cu(II),Cu(I)}}$  and  $E^{0'}_{\text{Cu(I),Cu(Hg)}}$  suggest that electrochemical reduction of methanol and ethanol solutions of Cu(II) at a platinum electrode should give two-step current-voltage curves. From current-voltage studies with a rotating platinum electrode, these values (*vs.* S.C.E.) for  $E^{0''}_{\text{Cu(II),Cu(I)}}$  and  $E^{0''}_{\text{Cu(I),Cu}}$  were obtained:

	$E^{0''}_{\text{Cu(II),Cu(I)}}$ slope	$E^{0''}_{\text{Cu(I),Cu}}$ slope
Methanol	+0.195 v. (0.052)	+0.135 v. (0.090)
Ethanol	+0.325 v. (0.111)	+0.265 v. (0.050)

$E^{0''}_{\text{Cu(II),Cu(I)}}$  and  $E^{0''}_{\text{Cu(II),Cu(I)}}$  differ only in the  $k$  values included in the potentials.  $E^{0''}_{\text{Cu(I),Cu}}$  is the potential which is related to the standard potential in the equation

$$E_{d.e.} = E^{0''}_{\text{Cu(I),Cu}} + 0.059 \log(i_d - i) \quad (16)$$

for the Cu(I),Cu wave. The agreement between  $E^{0'}_{\text{Cu(II),Cu(I)}}$  and  $E^{0''}_{\text{Cu(II),Cu(I)}}$  is not surprising, and in the light of the calculated, aqueous potentials<sup>5</sup>



the closeness of  $E^{0'}_{\text{Cu(I),Cu(Hg)}}$  and  $E^{0''}_{\text{Cu(I),Cu}}$  is also not altogether unexpected.

The practically identical values for  $E^{0'}$  and  $E^{0''}$  for the Cu(II),Cu(I) couple in both methanol and ethanol indicate that the approximation  $K^*_{\text{inst.}} = K_{\text{inst.}}$  used for the evaluation of  $E^{0'}$  values is valid.

From the potentials for the copper couples, the disproportionation constant for Cu(I) ion in both methanol and ethanol was calculated to be *ca.*  $1 \times 10^{-1}$ . Unlike aqueous solutions, dilute methanol and ethanol solutions of Cu(I) ion,

(5) See reference 3, p. 227, and W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 185.

therefore, are quite stable with respect to disproportionation of Cu(I) ion. The constant for the disproportionation reaction in water is  $1.7 \times 10^6$ . Because of the closeness of  $E^{0'}_{\text{Cu(II),Cu(I)}}$  and  $E^{0'}_{\text{Cu(I),Cu(Hg)}}$  one-step, instead of two-step, anodic-cathodic polarograms are observed for methanol and ethanol solutions of Cu(I) ion. The composite anodic-cathodic polarograms obtained are shown in Figure 1. Methanol and

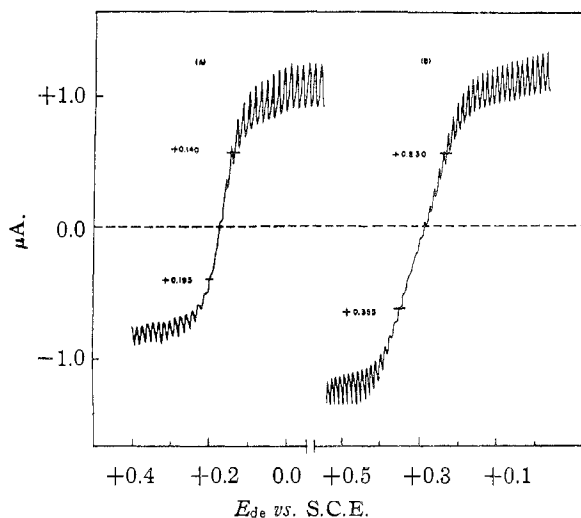


Fig. 1.—Composite anodic-cathodic polarograms of *ca.* 0.5 millimolar Cu(I) in methanol (A) and ethanol (B).

ethanol solutions of Cu(I) ion were prepared by diluting small volumes of deoxygenated nitromethane solutions of Cu(I) ion with deoxygenated methanol and ethanol.<sup>6</sup> Although the solutions were 2 and 6% by volume in nitromethane, the  $E_{1/2}$  values for the anodic and cathodic portions agree closely with the calculated values of  $E^{0'}_{\text{Cu(I),Cu(I)}}$  and  $E^{0'}_{\text{Cu(I),Cu(Hg)}}$ .

(6) Nitromethane solutions of Cu(I) ion were prepared by adding several pieces of copper foil to nitromethane solutions of  $\text{Cu(ClO}_4)_2$  and shaking. The solutions were checked polarographically for completeness of reduction. Cu(I) ion is not air oxidized in nitromethane; it is, however, rapidly air oxidized in methanol and ethanol