Xanthates as selective ligands for voltammetric study of Cu(II) in environmental samples

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ABSTRACT

Copper(II) in the presence of potassium n-propyl xanthate (Kpxan) and potassium cyclo hexyl xanthate (Kchxan) in ammonium chloride-ammonium hydroxide medium in the pH range 9.2 to 10.6 gives catalytic hydrogen waves at mercury electrode and the peak height is proportional to concentration of metal ion. The method developed is simple, rapid and sensitive without interferences of many metal ions and applicable to the analysis of alloys and agriculture materials. An electrode reaction mechanism based on d.c. polarographic and cyclic voltammetric results of the system is also suggested.   © 2008 Trade Science Inc. - INDIA

INTRODUCTION

In continuation of our earlier work on catalytic hydrogen currents (CHC) at mercury electrode due to complexation of organic thiocompounds with transition metal ions in ammonium chloride-ammonia supporting electrolyte[1-17] an attempt has been made with Cu(II)-xanthate systems. Potassium n-propyl xanthate(Kpxan) and Potassium cyclo hexyl xanthates(Kchxan) have been found to give catalytic hydrogen currents in the potential range -0.37 to -0.39V vs SCE with Cu(II) in NH_4Cl-NH_4OH medium in the pH range 9.2 to 10.6 (figure 1,2) . The quantitative experimental conditions have therefore been developed, the details of which are presented below (TABLE 1).

The mechanism of the catalytic hydrogen current is also a matter of importance because it is not well understood so far. An important technique, cyclic voltammetry, a key method for characterizing the adsorption at mercury electrode (HMDE) has been

Effectively utilized for suggesting the mechanism of Kinetic Brdicka Currents (CHC) of Cu(II)-xanthate systems in the present paper.

EXPERIMENTAL

Apparatus

The equipment used are d.c. Polarograph model CL-357 coupled with model LR-101 P strip chart re-

TABLE 1: Quantitative experimental conditions for Cu(II) determination through Cu(II)–xanthate catalytic hydrogen waves

Conditions	Kpxan	Kchxan
pH	9.6	9.2
NH_4Cl, M	0.3	0.3
Xanthate, mM	2.8	2.8
Copper(II), ppm	0.6-3.6	0.6-3.6

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a) 0.3 NH₄Cl, pH- 9.6, b) a + 2.8 mM Kpxan
c) a + 3.6 ppm Cu(II), d) b + 3.6 ppm Cu(II)
-V vs SCE
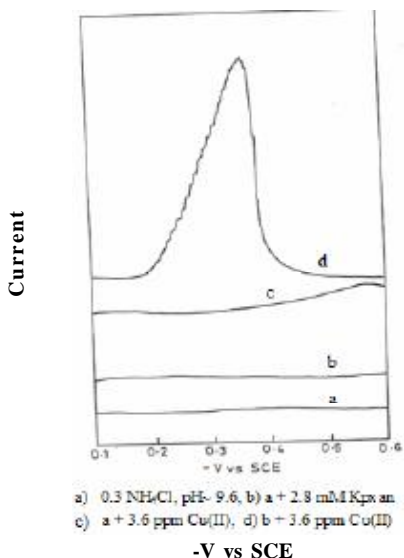
Figure 1: Polarographic curves of Cu(II)

a) 0.3 M NH₄Cl, pH ~ 10.0; b) a + 2.8 mM Kchxan
c) a + 3.6 ppm Cu(II);   d) b + 3.6 ppm Cu(II)
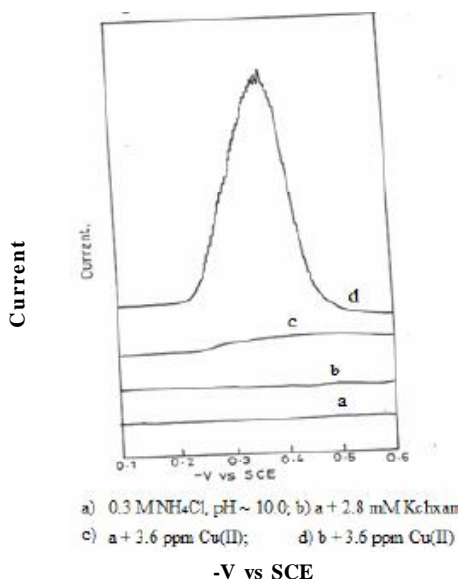-V vs SCE

Figure 2: Polarographic curves of Cu(II)

corder supplied by Elico Private Limited(Hyderabad, India), and Voltammograph model CV-27 coupled with R-XY recorder manufactured by BAS, U.S.A. The pH measurements are made by using pH meter, model LI-120(Elico Private Limited) with glass electrode of pH range 0-13. The temperature is maintained at 25 ± 0.2^{0}C and the flow of mercury at 3.8 seconds per drop.

Chemicals

All chemicals used are of Analytical Reagent grade unless specified otherwise. The solutions are prepared in double distilled water and diluted to required strength. 5% NH_4OH and 1% HCl are used for pH adjustments.

Gelatin and Triton X-100(S.d.fine.Chem. Ltd.) are pre-pared and diluted as per requirement. Kpxan and Kchxan are prepared and recrystallised according to standard procedures reported[18-21]. Standard proce-dure is used for preparing brass sample[22] and dry ash method[23] for agricultural materials for the preparation of the sample solutions.

RESULTS AND DISCUSSION

Effect of pH

Effect of pH on solutions containing 3.6ppm of cop-per in 0.3M ammonium chloride for both xanthates (2.8mM) were studied, varying the pH from 9.2 to 10.6 adjusting with ammonium hydroxide. With increasing pH the height of the catalytic wave increased and after attaining a maximum peak current (pH 9.6 for Kpxan and 10.0 for Kchxan) the wave height decreased with further increase in pH. The peak potential of the cata-lytic wave shifted towards positive potentials with in-crease in pH.

Effect of supporting electrolyte concentration

The effect of ammonium chloride in the range of 0.1 to 0.8M on the nature of current-voltage curves at DME for Cu(II)-xanthate complexes with two ligands have been studied, keeping the copper ion concentra-tion at 3.6 ppm and xanthates concentrations at 2.8mM adjusting pH 9.6 and 10.0, respectively.

The polarograms are well defined and the wave height is increased upto 0.3M NH_4Cl. The peak height decreased beyond this concentration and therefore 0.3M concentration is maintained for further studies. The peak potential of the catalytic wave shifts towards positive potentials with increase in ammonium chloride concentration.

Effect of reagent concentration

Solutions containing 3.6ppm of copper ion, 0.3M ammonium chloride are taken and the xanthates con-centration is varied from 0.6 to 3.6mM maintaining the pH of the solution at 9.6 in the case of Kpxan and 10.0 for Kchxan.

The wave height increased linearly with xanthate concentration upto 2.8mM for both Kpxan and Kchxan. With further increase in xanthate concentration the wave

height is independent of concentration and shows that the complex is stable.

Plot of{[Xan]/ip}vs[Xan]} is a straight line and confirms that adsorption phenomenon is involved in the electrode reaction process.

Effect of mercury pressure

The height of mercury column is varied and the polarograms of copper in quantitative experimental conditions are noted. It is found that $i_c/\sqrt{h}$ decreased with the height of the mercury column indicating that the current is catalytic in nature.

Effect of maximum suppressor

The effect of surface active substances, gelatin in the range 0.005 to 0.01% and Triton X-100, 0.002 to 0.004% on the catalytic wave height of Cu(II)-xanthate system is studied maintaining the fixed analytical concentrations for both xanthates. The catalytic wave decreased sharply upto 0.005% gelatin concentration and with further increase in concentration of the surface active material the wave height decreased by only about 2%. The peak potential shifted towards positive potentials and the catalytic peak became round shaped.

The suppression of the catalytic wave with 0.002 to 0.005% TX-100 is very small compared to gelatin. The peak potential shifted towards positive potentials in this case also.

Effect of copper (II) ion concentration on peak current

At fixed concentrations of xanthates[2.8mM] and ammonium chloride(0.3M) adjusting pH 9.6 and 10.0 respectively for two xanthates(Kpxan and Kchxan), the metal ion concentration is varied between 0.6 to 4.0ppm and the proportionality of peak current is studied.

The peak current increased linearly with copper concentration in the range 0.6 to 3.6 ppm and the corresponding calibration plot is shown in figure 3. The method suggests that the determination of micro amounts of copper is possible in unknown samples. It is observed that there is no change in the shape and the peak potential of the wave throughout the copper concentration range studied.
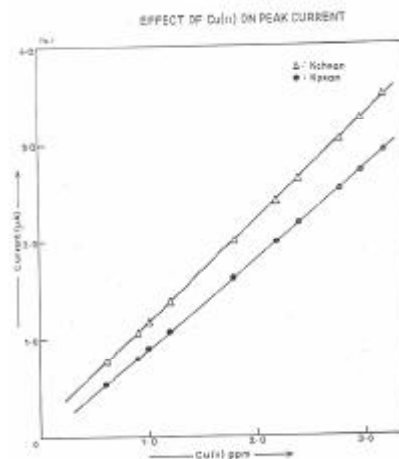
Effect of indifferent cations

Figure 3 : Effect of Cu(II) on peak current

The effect of neutral salts and replacement of monovalent cation with divalent cation leads to the changes both in the height and potential of the catalytic wave. Three alkali chlorides, potassium, sodium and lithium and bivalent cation, calcium are used. With increase in concentration of these metal chlorides the wave height decreased continuously and the decrease of wave height in calcium chloride is more compared to monovalent chlorides. The peak potential is shifted towards less negative potentials with all cations.

Interference studies

The effect of various metal ions on the catalytic wave of copper was studied. Most of the transition metal ions do not interfere under the conditions developed and Fe(II) and Ni(II) get precipitated which can be removed by filtration. The only metal ion, Mo(VI) interferes seriously by increasing the wave height and shifting the peak potential of copper catalytic wave.

Anions such as oxalate, citrate and EDTA interefere by completely suppressing the copper catalytic wave, where as nitrate interferes by increasing the catalytic wave height.

Electrocapillary curves

Elecrocapillary curves of NH_4Cl-NH_4OH supporting electrolyte (curve a) with 3.6 ppm of copper (curve b) and xanthate (curve c) and the complexes (curve d) are given in (Figures 4 and 5). From these curves it is observed that the electro capillary maximum is shifted to a more negative value and the drop time is suppressed to the positive side of the electro capillary maximum
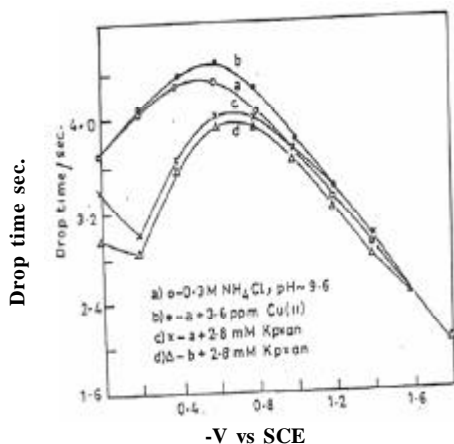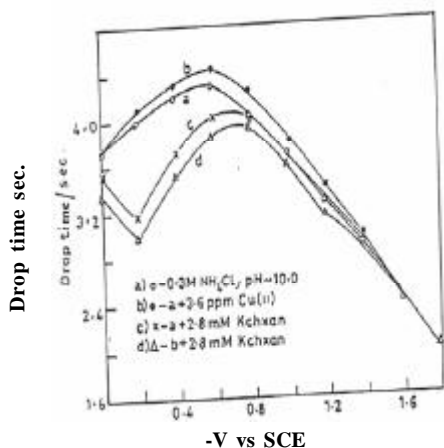
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-V vs SCE

Figure 4: Electrocapillary curves

-V vs SCE

Figure 5 : Electrocapillary curves
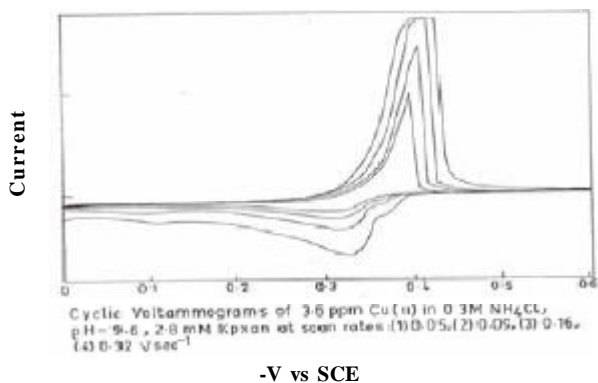

-V vs SCE

Figure 6:Cyclic voltammograms of Cu(II)

where xanthate ions are strongly adsorbed(curve c). The Cu(II)- xanthate complex further suppresses the positive branch of the electro capillary curve indicating that adsorption is involved in the reaction process of catalytic wave. Complete desorption of xanthate as well as its complex occurs at potentials more negative than
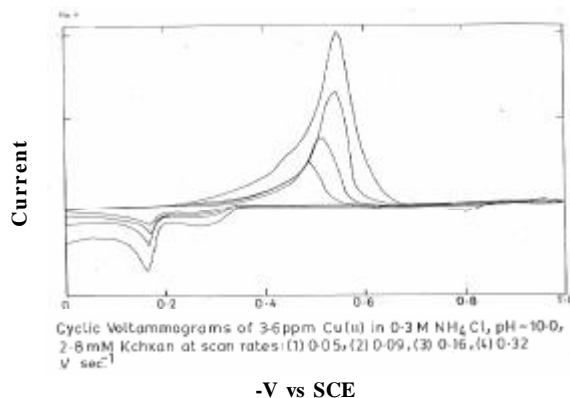

-V vs SCE

Figure 7:Cyclic voltammograms of Cu(II)

TABLE 2:Effect of scan rate on copper(II)-Kpxan system

S.no	Scan rate, v/Sec	Epc, -V Vs SCE	Ipc, μA	Ipc/$\sqrt{V}$	Epa, -V Vs SCE	Ipa, μA
a	0.05	0.40	6.00	27.27	0.320	1.10
	0.09	0.41	7.00	23.33	0.327	0.40
	0.16	0.41	8.00	20.00	0.328	0.80
	0.32	0.41	10.00	17.85	0.332	1.00
b	0.05	0.42	5.00	22.72	0.320	0.20
	0.09	0.42	6.00	20.00	0.330	0.30
	0.16	0.43	7.00	17.50	0.340	0.40
	0.32	0.43	9.00	16.07	0.342	1.00
c	0.05	0.41	4.00	18.18	0.330	0.30
	0.09	0.42	5.00	16.66	0.340	0.40
	0.16	0.42	6.00	15.00	0.350	0.42
	0.32	0.43	8.00	14.28	0.354	1.20

(a) 3.0ppm Cu(II):0.3M NH$_4$Cl:pH 9.6:2.0mM Kpxan; (b) 3.0ppm Cu(II):0.3M NH$_4$Cl:pH 9.6: 2.8 mM Kpxan; (c) 3.6ppmCu(II):0.3M NH$_4$Cl:pH 9.6:2.8mM Kpxan

that of the electro capillary maximum where all the curves coincide (curve a, c and d).

Cyclic voltammetry of Cu(II) xanthate

Cyclic voltammetry of Cu(II)-xanthate complexes showed a wave on the cathodic side at about -0.41V Vs SCE for Kpxan and -0.49V Vs SCE for Kchxan. These waves depend markedly on voltage scan rate, and concentration of the complex(Figures 6,7).

The cyclic voltammogram indicates that the reactant, Cu(II)-xanthate complex is weakly adsorbed on the stationary electrode which is seen on enhancement of cathodic peak current compared to the reverse anodic peak current. With increase in scan rate, the current function decreased and peak potential shifted to negative values(TABLE 2,3).

The peak on the reverse scan at -0.32 V with Kpxan and at -0.183 V Vs SCE with Kchxan are at more

TABLE 3 : Effect of scan rate on Cu(II)-kchxan system

S.no.	Scan rate, ν/sec	Epc, -V vs SCE	Ipc, μA	Ipc/√V	Epa, -V vs SCE	Ipa, μA
a	0.05	0.490	4.00	18.18	0.180	0.5
	0.09	0.491	5.00	16.66	0.182	1.0
	0.16	0.492	6.00	15.00	0.183	2.0
	0.32	0.493	8.00	14.28	0.184	3.0
b	0.05	0.490	5.00	22.72	0.180	0.5
	0.09	0.500	6.00	20.00	0.183	2.0
	0.16	0.510	7.00	17.50	0.184	3.0
	0.32	0.520	9.00	16.07	0.185	4.0
c	0.05	0.500	6.00	27.27	0.181	1.0
	0.09	0.510	7.00	23.33	0.183	2.0
	0.16	0.520	8.00	20.00	0.184	3.0
	0.32	0.530	10.00	17.85	0.186	4.0

(a) 3.0ppm Cu(II):0.3M NH_4Cl: pH 10.0:2.2mM Kchxan; (b) 3.0ppm Cu(II):0.3M NH_4Cl:pH 10.0:2.8mM Kchxan; (c) 3.6ppm Cu(II):0.3M NH4Cl:pH 10.0:2.8mM Kchxan

TABLE 4 : Determination of copper in eluesine coracana (Finger millet)

	(a) Kpxan	(b) Kchxan
Xanthate, mM	2.8	2.8
NH4Cl, M	0.3	0.3
pH 9.6 10.0	9.6	10.0

* Sample/ Xanthate	Cu(II) added, ppm		Cu(II) in the whole sample, ppm	
	ppm	Total**found	Catalytic method	AAS method
a	1.0	1.624	12.48	
b	1.0	1.625	12.50	12.50

*5ml of the sample solution is used; **Average of five individual determinations

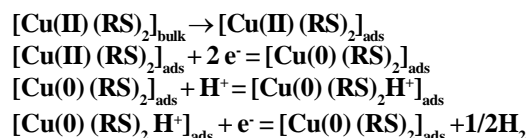**TABLE 5 : Determination of copper in brass [Certified amount of Cu (%)=67.4]**

	(a) Kpxan	(b) Kchxan
Xanthate, mM	2.8	2.8
NH4Cl, M	0.3	0.3
pH	9.6	10.0

* Sample/Xanthate	Cu(II) in the sample, ppm	
	Catalytic method	AAS method
a	67.2	67.3
b	67.3	67.3

*5ml of the sample solution is used; **Average of five individual determinations

anodic potentials compared to their respective cathodic peaks. This may be due to increase in free energy of adsorption and therefore the adsorbed reactant is more difficult to reduce and reduction occurs at more cathodic potential and only one peak observed[24] unlike other metal xanthates reported earlier.

Mechanism of copper (II) xanthate catalytic hydrogen wave

The characteristic nature of the wave/peaks observed in d.c. polarography and cyclic voltammetry suggest that the catalytic hydrogen waves are of Brdicka type and the reaction mechanism may be represented as shown below.

$$[Cu(II) (RS)_2]_{bulk} \rightarrow [Cu(II) (RS)_2]_{ads}$$
$$[Cu(II) (RS)_2]_{ads} + 2 e^- = [Cu(0) (RS)_2]_{ads}$$
$$[Cu(0) (RS)_2]_{ads} + H^+ = [Cu(0) (RS)_2 H^+]_{ads}$$
$$[Cu(0) (RS)_2 H^+]_{ads} + e^- = [Cu(0) (RS)_2]_{ads} + 1/2 H_2$$

Application of the catalytic method to real samples

The catalytic polarographic method of Cu(II) using Kpxan and Kchxan as reagents is extended to the analysis of leafy vegetables and alloys.

Leafy vegetables

3.5g of Eluesine Coracana is collected and digested by dry ash method. The ash is dissolved by heating with 10ml of 2N HCl, filtered through an acid washed membrane filter and the residue is washed with hot water. Standard addition method is used in this case (TABLE 4).

Alloy

Standard sample of Brass is brought into solution by standard procedures.

Aliquots of the above sample solution are taken and quantitative experimental conditions are maintained and the solutions are polarographed.

The results obtained by this method are further supported by AAS method (TABLE 5).

CONCLUSIONS

The presence of xanthate in a medium containing ammonium chloride-ammonium hydroxide supporting electrolyte and copper (II) gives rise to a catalytic hydrogen wave, positive to the Cu(II) reduction wave. The effect of pH and ammonium chloride concentration clearly indicate the characteristic property of catalytic surface reactions.

The height of the catalytic wave is found to vary linearly with the concentration of xanthate at low concentration and at higher concentrations the variation shows a parabolic form. The non-linear portion has the shape of a curve resembling a Langmuir adsorption isotherm and therefore the plot of {[Xanthate]/ip} vs {Xan-

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thate} is a straight line[25,26]. This dependence is due to the adsorption of the catalytically active compound at the electrode surface.

The height of the catalytic wave decreases slightly with the increase in gelatin and Triton X-100 concentration and suggest that the adsorption is involved in the mechanism of the catalytic wave. The surfactants decrease the free area of the electrode and so decrease the height of the catalytic hydrogen wave. The adsorption phenomenon is further supported from the study of indifferent electrolyte effect where the catalytic current decreased more with increasing ionic strength of Ca^{2+} than in the presence of K^+ or Na^+ or Li^+ indicating Brdicka type of Catalytic currents[27]. The shapes of the electro capillary curves confirm the adsorption of copper xanthate complex on the mercury surface[28]. The linear increase in peak current with Cu(II) is indicative of diffusion controlled currents.

All these observations clearly indicate that the catalytic current is of Brdicka type. When current is less than 20% of its limiting value it is entirely kinetic in nature and at maximum or limiting current or saturation value it is diffusion controlled[29]. The peak height of this increased with the complex concentration as well as with scan rate, indicative of adsorption.

ACKNOWLEDGMENTS

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