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EFFECT OF COUNTERION, SOLVENT AND LIGAND SUBSTITUENTS ON THE REDUCTION POTENTIALS OF COPPER (II) COMPLEXES OF VARIOUS IMIDAZOLES IN SOME NONAQUEOUS SOLVENTS

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ABSTRACT

The reduction potential of copper (II) complexes with various imidazole (L) = imidazole (1mH), 2-methylimidazoles (2-MeIm), 1,2-dimethylimidazole (1,2-$M_2$1m) and benzimidazole(B_zIm) in 1:10 and 1:100 [Cu(II)]:[L] molar ratios, 1 x 10^{-3}M CuX_2. nH_2O (X = ClO_4, NO_3^-, Cl^-, Br^-, in dimethyformamide(DMF)/0.1M Tetrabutylammonium perchlorate (TBAP) shows identical set of reduction potentials in 1:100 molar ratio for ClO_4^-, No_3^-,Cl^-, Br^-, counterions for a given imidazole. However, for 1:10 molar ratio, reduction potentials for Cl^-, Br^- are more positive as compared to CLO_4^-/NO_3^- set. The catholic potential of Cu (II) - B_zIm systems with 1:2, 1:4, 1:6, 1:10 and 1:100 molar ratios, 1 X 10^{-3}M $CuCl_2$. $2H_20$ in DMF, Dimethylsufoxide (DMS0), acetonitrile (AN), and ethylalcohol/ 0.1M TBAP depends on both the interaction of solvent and counterion to reactant species and reduction product and the structures of these copper (II) and copper (I) complex species. In the copper (II) – ligand system with [Cu(II)]: [L] = 1:2, 1:4, 1:6, 1:10 and 1:100 molar ratios, 1 x 10^{-3}M $CuCl_2$. $2H_2O$ in DMF/0.1M TBAP, based on the pka values of the ligands, the reduction potential increases in the order 1mH > 2-MeIm >1,2-Me_2Im > B_zIm.

KEYWORDS: Counterion, Solvent, Substituents, potentials, voltammograms.

INTRODUCTION

The influence on redox potentials by the interacting effects of axially bound solvent molecules and axially coordinated monovalent anions has been reported for Fe (III) [Bottomley and et. al. 1981; Bottomley et al 1980; Kadish, et al 1978] and Mn (III) [Bottomley et al., 1982]. In non coordinating nonaqueous solvents, the reduction of TPPFeX [Fe(III)→ Fe(II), (TPP = tetraphenylporphyrin) becomes more difficult as the counterion varies from weakly coordinating ClO_4^- anion to tightly bound F^-anion. Similarly half wave potentials for electroduction of TPPMnX in CH_2Cl_2 have shown that Mn (III) is preferentially stabilized [Botomley et al, 1982] over Mn (II) as the counterion is varied between ClO_4^- and the tightly coordinated N_3^-. The potential range over which this affect is operative depends greatly on the nature of the central metal.

The paper therefore is a result of cyclic voltametric investigation of effect of counterion, solvent and ligand substituents on the reduction potentials of copper (II). Complexes of various imidazoles.

MATERIAL AND METHODS

MATERIAL

The reduction potentials were obtained with a BAS Model CV-IB (Indiana USA) cyclic voltammograph instrument having an electrochemical cell with a three electrodes system. The working electrode was a glassy carbon electrode (GCE). Platinum wire was used as an auxiliary electrode, while a saturated calomel electrode (S. C. E.) as reference electrode with E^o = 0.242V vs NHE. The voltammograms were recorded on an X – Y recorder. B_zIm, 2-MeIm, I, 2-Me_2Im, ImH and TBAP were obtained from Aldrich (USA). DMSO, AN, DMF were spectroscopy grade and were used as obtained. Ethylalcohol was supplied by Calcutta chemical company, India. The copper salts were of analytical reagent grade.

METHOD

General: All solutions scanned for voltammograms, were prepared so as to observed the various effects on the first reduction potential of the copper (II) complexes. All the cyclic voltammetric experiments scanned from + 0.80V + 0.20V were done in an inert atmosphere achieved by purging the cell solutions with nitrogen gas for about 20 minutes and maintained over the cell solution during the recording of the voltammograms. The nitrogen gas was purified by bubbling through alkaline vanadous sulphate solution and passing through a calcium sulphate drying tube before bubbling through the cell solution(s). The experiments were carried out at 25° ± 1°C in 0.1M TBAP supporting electrolyte. The experiments were carried out with freshly prepare solutions.

Counterion Effect: A stock solution of 0.01M in 100cm^3 solvent was prepared for $Cu(ClO_4)_2.6H_2O$, $Cu(NO_3)_2.6H_2O$, $Cu(ClO_4)_2.6H_2O$, $Cu(NO_3)_2.6H_20$, $CuCl_2.2H_20$ and $CuBr_2.H_20$. For a total working volume of 20cm^3, 2.0cm^3 solution was used for 0.001M of each copper salt. 0.01M and 0.1M imidazole (ImH) was prepared by placing 0.136g and 1.361g with respective 2.0cm^3 copper salt solution in a clean dry beaker and made up to 20cm^3 and stirred for clear solution. This is specified as 1:10 and 1:100 copper: ligand molar ratio. All solutions were prepared in DMF.

Solvent Effect: Stock solutions of 0.01M in 100cm^3 solvent was prepared for $CuCl_2.2H_20$ and B_zIm in DMSO, AN, Absolute alcohol and DMF respectively. For a total working volume of 20cm^3, 2.0cm^3 of $CuCl_2.2H_2O$ was placed in a clean dry beaker for each experiment. For 0.002M, 0.004M and 0.006M B_zIm, 4.0cm^3, 8.0cm^3 and 12.0cm^3 respective were mixed with copper (II) solution in the same beaker and made up to 20cm^3 with respective nonaqueous solvents. 0.01M and 0.1M B_zIm was prepared by dissolving 0.236g and 2.362g in a beaker containing 2.0cm^3 $CuCl_2.2H_2O$ and made up to 20cm^3 with respective non-aqueous solvents. These are specified as 1:2, 1:4, 1:6, 1:10 and 1:100, copper: ligand molar ratio.

Ligand substituent effect: The stock solution of $CuCl_2.2H2O$ prepared for solvent effect was used and the same procedure for solvent effect was also used to prepare 0.002M, 0.004M, 0.006M of all ligands from a stock solution of 0.01M. For 1:10, 1:100 molar ratio, 0.136g and 1.362g for 1mH, 0.164g and

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1.642g for 2-MeImH, 0.1923g and 1.923g for 1, 2Me$_2$1mH, 0.236g and 2.362g for B$_z$Im were weighed and solution prepared as in solvent effects, except that solvent for all solutions in this case was DMF while the total working volume remained as 20cm^3.

RESULT AND DISCUSSION

Counterion Effect: Table 1 shows that in [Cu(II): [L] = 1:100 molar ratio, almost identical set of potentials (Epc) are observed for all countermonoanions (ClO^{-4}, NO$^-_3$, Cl$^-$, Br$^-$) for a given imidazole, strongly suggesting that either the anions are not coordinated to the central metal ion or the anions are displaced by solvent molecule giving the initial complex as hexadented electroactive species of [Cu (ImH)$_4$.(solvent)$_2$]$^{2+}$.2x.

On the other hand, in 1:10 molar ratio, the reduction potentials (Epc), Table 1, shows ClO$_4^-$ and NO$_3^-$ complexes with a given imidazole to be almost similar. However, reduction potentials are also similar for Cl$^-$ and Br$^-$ complexes but are more positive as compared to those of ClO$_4^-$/NO$_3^-$ set. This indicates that the initial reactant species are not similar for these two sets of ClO$_4^-$/NO$_3^-$ and Cl$^-$/Br$^-$ complexes.

Table 1: Cyclic Voltammetric Parameters for Copper (II) Complexes with various imidazoles, 1 x 10^{-3}MCuX$_2$. nH$_2$0/DMF, at v = 25Mv/s.

Copper (II) Salt	[Cu(II)]: [L]	Epc/mV	Eo/mV	ΔEp/mV
L = 1mH				
Cu(ClO$_4$)$_2$.6H$_2$0	1:10	+100	+145	90
	1:100	+ 10	+45	70
Cu(NO$_3$)$_2$.6H$_2$0	1:10	+105	+150	90
	1:100	+ 5	+40	70
CuCl$_2$.2H$_2$0	1:10	+170	+223	105
	1:100	+ 10	+45	70
CuBr$_2$.H$_2$0	1:10	+175	+228	105
	1:100	+ 5	+45	80
L = 2- MeIm				
Cu(ClO$_4$)$_2$.6H$_2$0	1:10	+185	+240	110
	1:100	+110	+155	90
Cu(NO$_3$)$_2$.6H$_2$0	1:10	+210	+253	85
	1:100	+110	+153	85
CuCl$_2$.2H$_2$0	1:10	+220	+265	90
	1:100	+105	+150	90
CuBr$_2$.H$_2$0	1:10	+225	+270	90
	1:100	+115	+155	80
L = 1,2, Me$_2$Im				
Cu(ClO$_4$)$_2$.6H$_2$0	1:10	+225	+280	110
	1:100	+135	+187	105
Cu(NO$_3$)$_2$.6H$_2$0	1:10	+230	+285	110
	1:100	+135	+185	105
CuCl$_2$.2H$_2$0	1:10	+240	+303	125
	1:100	+135	+185	100
CuBr$_2$.H$_2$0	1:10	+230	+310	135
	1:100	+135	+185	100
L = B$_z$Im				
Cu(ClO$_4$)$_2$.6H$_2$0	1:10	+230	+277	95
	1:100	+155	+197	85
Cu(NO$_3$)$_2$.6H$_2$0	1:10	+235	+282	95
	1:100	+155	+197	85
CuCl$_2$.2H$_2$0	1:10	+300	+348	95
	1:100	+165	+210	90
CuBr$_2$.H$_2$0	1:10	+325	+375	100
	1:100	+185	+230	90

Furthermore, a comparison of reduction potentials for 1:10 and 1:100 Cu (II) – imidazole systems for a given ligand (L) and counterion shows a potential shift of ≅ 90 mV in the cathodic direction in the latter case. This is an indication that the reactant species are also not similar in 1:10 and 1:100 molar ratios, probably some lower Cu (II)-imidazole species [Bonomo et al, 1988] like Cu (imH)$_3^{2+}$ may be formed in the former case. Contrary to ones expectation, reduction potentials observed for 1:10 copper (II) – ligand system with a particular imidazole involving various anions (ClO$_4^-$, NO$_3^-$, Cl$^-$, Br$^-$) indicate that the reduction of copper (II)-imidazole complexes with weakly coordinating ClO$_4^-$/NO$_3^-$ counter-anions is more difficult as compared to those involving tightly bound Cl$^-$/Br$^-$ counter ions. This clearly demonstrates the interacting effects of solvents and counter ions on the electrode reactions of copper (II) and copper (I)-imidazole complexes with respect to ClO$_4^-$, NO$_3^-$ anions.

Solvent Effect: A close look at Table 2 clearly shows that the reduction potential of the copper (II) B$_z$Im complexes with Cl$^-$ counterion at a given ratios are dependent on the nonaqueous solvent.

Table 2: Cyclic Voltammetric Parameters for Copper (II) - B$_z$Im Complexes, 1 x 10^{-3}M CuCl$_2$ 2H$_2$0 in various Nonaqueous solvents at v = 25mV/s.

Solvents	[Cu(II)]: [Bz/m]] Molar ratio	Epc/mV	E^o/mV	ΔEp/mV
DMSO	1:2	+260	+313	105
	1:4	+240	+300	120
	1:6	+230	+283	105
	1:10	+225	+280	110
	1:100	+120	+165	90
AN	1:2	+365	+435	140
	1:4	+325	+375	100
	1:6	+305	353	95
	1:10	+265	+313	95
	1:100	+140	+183	85
Absolute alcohol	1:2	+350	+410	120
	1:4	+320	+377	115
	1:6	+295	+350	110
	1:10	+275	+325	105
	1:100	+165	+223	115
DMF	1:2	+375	+423	95
	1:4	+340	+390	100
	1:6	+315	+365	100
	1:10	+300	+348	95
	1:100	+165	+210	90

The reduction potentials observed for different [Cu (II)]: [B$_z$Im] molar ratios shift anodically in the following order:

(i) 1:2 molar ratio: DMSO<ethylalcohol<AN<DMF
(ii) 1:4 molar ratio: DMSO<ethylalcohol~AN~DMF
(iii) 1:6 molar ratio: DMSO<ethylalcohol<AN<DMF
(iv) 1.10 molar ratio: DMSO<AN<ethylalcohol<DMF
(v) 1:00 molar ratio: DMSO<AN<ethylalcohol~DMF

The donor number (donocity) of these solvents increase in the order AN (14.1)<ethylalcohol (-)<DMF (26.6)<DMSO(29.8). (Bertini 1967; R. V. Gutmann 1967]. On the basis of donor number of these nonaqueous solvents, it is expected that the reduction potential of the copper (II) – benzimidazole complex in DMSO should be most negative [Bottomley et al 1982] while that in AN should be most positive [Bottomley et al 1982]. However, the observed trends are different from the expected one, thus suggesting that the reduction potential not only depends upon the coordination of solvent molecule(s) versus the counteranion to the reactant Cu (II) species and the reduction product Cu(I) species but also the structures of these copper (II) and copper (I) complex species [Bottomley et al 1981]. It could be concluded therefore that the solvent dependence on the first reduction potential (Epc$_1$) for copper (II) – benzimidazole –chloro complexes is complicated.

Ligand Substituents Effect: The pka [Kolks et al, 1982] of the neutral form of the ligands increase in the sequence: B$_z$Im (5.4) < ImH (6.95)<2-MeIm (7.75)<1,2-Me$_2$Im (9.79). The strength of a metal-ligand bond as reflected in the stability constants of the reaction M+nL → MLn, is directly correlated with ligand basicity (pka) as has been frequently been observed [Martell and Carlin, 1952, Cowgill and Clark, 1952] and theoritical calculations [Bhattacharyya, 1980] support this trend.

The methyl group (s) (a σ-donor) in the 2-MeIm and 1,2 – Me$_2$1m increases the electron density on the nitrogen atoms of the ligands [Kadish and Bottomley, 1980; March, 1988] with respect to the ImH. The reverse argument applies for the σ-withdrawing fused benzene ring of the B$_z$1m. Because 1, 2 – Me$_2$Im is most basic amongst these imidazole ligands, the increased electron density at the core nitrogens would be expected to result in the most difficult reduction of the copper (II) – 1, 2 – Me$_2$Im complex [Sundberg and Martin 1974]. Reverse argument applies for copper (II) – benzimidazole complexes. On the basis of basicity (pka) of these ligands alone, on expects that the reduction potentials of the copper (II) complexes with these imidazole ligands should become more positive in the order: 1,2 → Me$_2$Im → 2-MeIm → 1mH → B$_z$Im. However, the observed reduction potentials at a given M:L ratio increase in the order. ImH → 2-MeIm → 1,2 – Me$_2$Im → B$_z$Im (Table 3).

Table 3: Cyclic Voltammetric Parameters for Copper (II) – Complexes with various imidazoles, 1 x 10^{-3}M $CuCl_2.2H_2O$ in DMF at v = 25mV/s.

Ligand	[Cu(II)]: [L] Molar ratio	Epc/mV	E°/mV	ΔEp/mV
1MH	1:2	+260	+328	135
	1:4	+235	+288	105
	1:6	+200	+250	100
	1:10	+170	+223	105
	1:100	+10	+45	70
2-Me/m	1:2	+315	+370	110
	1:4	+275	+322	95
	1:6	+255	+302	95
	1:10	+220	+265	95
	1:100	+105	+150	90
1,2-Me_2Im	1:2	+325	+403	155
	1:4	+285	+348	125
	1:6	+270	+338	130
	1:10	+240	+185	125
	1:100	+135	+303	100
B_2Im	1:2	+375	+423	95
	1:4	+340	+390	100
	1:6	+315	+365	100
	1:10	+300	+348	95
	1:100	+165	+210	90

This deviation from the expected trend based on pka values is attributed to the dominance of steric effects [Nozaki et al, 1957, Meek and Ehrhard, 1965] over the inductive effects in the case of 2-MeIm and 1,2 – $Me_2$1m ligands. Mandal and Nag (1986) have reported that reduction E1/2 values of copper (II) complexes increase with increase in pka values of ligands.

CONCLUSION

This investigation reveals that the effect of counterion, solvent and ligand substituent on the reduction potentials of copper (II) complexes is complicated and not as straight forward as one would have expected.

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