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Sensitive determination of Iron (II) using catalytic hydrogen wave in the presence of amino compounds at DME

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ABSTRACT

A simple and sensitive catalytic polarographic method for the determination of Iron is developed based on the catalytic currents of Iron (II)-amine complex in the presence of NH4Cl – NH4OH medium at pH~7.8. The Iron (II) produces a catalytic hydrogen wave at -1.26 V vs SCE with n-butyl amine in NH4Cl–NH4OH medium. The peak height is proportional to metal ion Concentration. The proposed method is free from interference to many metal ions except molybdenum and is sensitive up to 0.1 ppm. The developed method is applied for the determination of Iron (II) in drinking water samples, agricultural materials and pharmaceutical samples.

KEYWORDS

Catalytic hydrogen waves;
Iron (II);
n-Butyl Amine;
Environmental samples;
Pharmaceutical samples.

INTRODUCTION

Catalytic hydrogen waves due to organic thio compounds with xanthate in the presence of Fe(II) at DME have been reported[1,2] from these laboratories.

Catalytic hydrogen currents of metal ions with amines have also been suggested[3] but so far there is no reference available on this. In our attempts on catalytic hydrogen currents due to their diagnostic criteria and high sensitive nature, n-butyl amine has been tried with Fe (II).

n-butyl amine (nBA) gives complexes with Fe (II) and is found to give catalytic hydrogen currents at DME at the peak potential - 1.26 V vs SCE in NH4Cl – NH4OH medium at pH 7.8 (Figure 1) . The quantitative experimental conditions have been developed and the details are shown in TABLE 1.

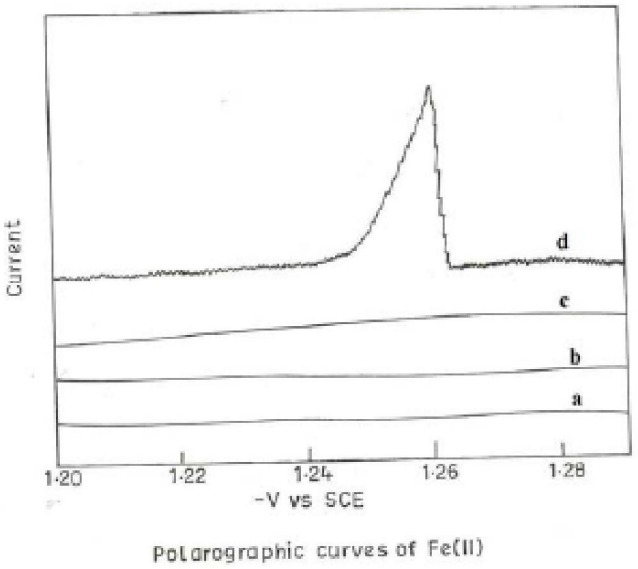

Figure 1 : Polarographic Curves of Fe(II)

a) 0.4 MNH4Cl, pH~7.8. **b) a + 0.2 mM nBA**

c) a + 3.0 ppm Fe (II) **d) b + 3.0 ppm Fe (II)**

TABLE 1 : Quantitative experimental conditions for Fe (II) determination through Iron (II)-n-butyl Amine catalytic hydrogen waves

conditions	Optimum values
pH	7.8
NH_4Cl, M	0.4
Amine, mM	0.2
Iron(II), ppm	0.1 – 10.0

EXPERIMENTAL

Reagents: All chemicals used are of analytical reagent grade only. The solutions are prepared in double distilled water and diluted to required strength. 5% NH4OH and 1% HCl is used for pH adjustments. Gelatin and Triton X-100 are prepared and diluted as per requirement. N-Butyl amine (S.d. fine-chemicals Ltd.) solution is used.

Water samples are preconcentrated by evaporation and standard addition method is used for analysis. Dry ash method[4] is used for agricultural products.

Apparatus: The equipment used is d.c polarograph model CL-358 coupled with model LR-101 P strip chart recorder supplied by Elico Private Limited (Hyderabad, India). 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 2.5 s per drop.

Preparation of Fe (II) in Environmental & Pharmaceutical Samples

Drinking water samples: One liter of the samples collected from Kalyani Dam, Bore wells of Tirupati town, Chittoor district, India are preconcentrated to 100ml.

Agricultural materials: 5g of piper betle (betle leaves) and 5 g of Murraya koenigii (Curry leaves) are collected from Tirupati town, Chittoor District are digested by dry ash method and brought into solution (5 g piper betle leaves/500 mL and 5 g curry leaves/50 mL double distilled water).

Pharmaceuticals: Feefol and Feonat capsules from E.S. Kayef Limited and Natco Fine Pharmaceuticals Pvt. Ltd. containing iron in the form of ferrous sulphate have been selected to estimate the iron content in the composition as given by the manufacturers. The capsule is digested and brought into 1-liter solution.

RESULTS AND DISCUSSION

Effect of pH

The concentration of metal ion 3.0 ppm, ligand 0.2mM/Amine and ammonium chloride 0.4 M are fixed and the pH effect is studied from 6.0 to 10.0 adjusting with hydrochloric acid or ammonium hydroxide. A well-defined wave is obtained at pH 7.8 with amine. At higher pH values, the wave height is diminished. The pH where the catalytic wave height is maximum and wave is well defined is selected as the optimum pH (7.8) for all other studies. With increase in pH, the peak potential of the catalytic wave shifted towards more negative potentials upto the optimum pH and with further increase in pH, the shift in peak potential is small.

Effect of Supporting Electrolyte

The wave height of the catalytic hydrogen wave is not only dependent on pH but also on the buffer capacity. Ammonium chloride concentration is varied between 0.1 to 0.6 M maintaining the metal ion concentration at 3 .0 ppm, amine concentration at 0.2 mM and adjusting the pH of the solution with ammonium hydroxide to pH 7.8. The wave height increased upto 0.4 M and decreased beyond this concentration. Hence, 0.4 M ammonium chloride concentration is fixed as the analytical concentration of the supporting electrolyte for all studies. The peak potential of the catalytic wave shifted considerably towards negative potentials with increase in ammonium chloride concentration.

Effect of Reagent Concentration

The Polarogram of iron (II) – amine complexes over a wide range of ligand concentration from 0.1 to 0.8 mM are recorded maintaining the concentration of iron (II), ammonium chloride and pH at their optimum values as mentioned above. The results reveal that the peak height is maximum when amine concentration is 0.2 mM and this concentration is selected as the optimum value for all other studies. The amine concentration shifts the peak potential towards more negative values. The variation of the wave height as a function of amine concentration is not linear and tends to a limiting value, which

is a characteristic property of catalytic wave.

The catalytic behavior of iron-amine complex is further supported by the effect of mercury height on the peak current and temperature coefficient values. The catalytic current decreased with increase in mercury pressure and ic/vh is found to decrease. The wage height increased up to 30^0. The value of temperature coefficient is less indicating that the current is catalytic in nature.

Gelatin and Triton X-100 suppressed the peak by 10 to 25% upto 0.005 and 0.002% respectively and remained almost constant over and above these concentrations. The shift in peak potential is also small towards negative potentials through the concentration effect studied.

Effect of iron (II) on peak current

In order to obtain concentration range over which the catalytic wave is proportional to the metal ion, Fe (II) is changed from 0.1 to 10.0 ppm in the quantitative experimental conditions and the solutions are polarographed. The peak current increased proportionally with iron (II) over concentration range 0.1 to 10.0 ppm. The lowest detection limit is 0.1ppm.

Interference studies: Zn (II) interferes with Fe (II) and is masked by adding 2 ml of 2% sodium tartrate solution whereas Mo (VI) increases the height of the catalytic wave of Fe (II) shifting the peak potential towards more negative value and making the determination of Fe (II) impossible.

Anions such as oxalate and carbonate interfere with Fe (II) by suppressing the catalytic wave by 40% whereas EDTA interferes severely by suppressing the catalytic wave totally.

Effect of Indifferent cations

The effect of neutral salts on the iron (II)-amine system is studied using lithium, sodium, potassium and calcium chlorides, keeping NH4Cl in the solution constant at 0.4 M and corresponding pH value. The wave height decreases continuously with increase in the concentration of NaCl and KCl. The decrease in height is more with LiCl and is much more with CaCl2. The peak potential is shifted towards less negative potentials with increase in electrolyte concentration.

Electrocapillary curves

The presence of amine in NH4Cl solution decreases the drop time of the DME to an appreciable extent on the positive side of the electrocapillary maximum and the electrocapillary maximum is shifted to a more negative value. Iron (II)–Amine complex further suppresses the positive branch of the electrocapillary curve indicating surface phenomenon in the reaction process. This requires further confirmation by cyclic voltammetry and the work is in progress.

Applications of the catalytic method

The method adopted for the analysis of iron content in water samples and leafy vegetables is standard addition method. The results obtained by catalytic hydrogen currents are further supported by atomic absorption spectrophotometric method given in TABLE 2, 3 and 4.

The results indicate that the drinking water samples contain low levels of iron (II) within the tolerance limits (TABLE 2). The leafy vegetables grown in the nearby villages of Tirupati town show that iron is present in the samples, but within the limits of standard values reported (TABLE 3). Drugs also confirm the manufacturer's values (TABLE 4).

TABLE 2 : Determination of Iron (II) in water samples
NH4Cl, M : 0.4 Amine, mM : 0.2 PH : 7.8

Sample*	Fe (II), ppm		Fe (II) in the sample, ppm	
	added	Total found**	Catalytic method	AAS method
Kalyani Dam water	0.5	0.617	2.34	2.62
	0.5	0.628	2.57	
Bore well water	0.5	0.832	6.64	6.80
	0.5	0.843	6.85	

***5ml of concentrated sample is used.**
****Average of five individual measurements**

TABLE 3 : Determination of Iron (II) in agricultural materials
NH4Cl, M : 0.4 Amine, mM : 0.2 PH : 7.8

Sample*	Fe (II), ppm		Fe (II) in the sample, ppm	
	added	Total found**	Catalytic method	AAS method
Piper betle	0.5	1.475	97.50	98.30
	0.5	1.480	98.00	
Murraya koenigii	0.5	1.323	8.23	
	0.5	1.328	8.28	8.32

***1ml of solution is used.**
**** Average of five individual measurements**

TABLE 4 : Determination of Iron (II) in drugs
NH4Cl, M : 0.4 Amine, mM : 0.2 PH : 7.8

Sample*	Iron in capsule (g)	Fe (II) in the sample**,(g)	
		Catalytic method	AAS method
Feefol (E.S.Kayef Ltd., India)	Ferrous sulphate 0.15	0.1492 0.1491	0.1495
Feonot (Nath Fine Pharmaceuticals Pvt., India)	Ferrous sulphate 0.15	0.1419 0.1485	0.1500

***1ml of solution is used.**
****Average of five individual measurements**

CONCLUSIONS

The polarographic reduction of iron (II) in aqueous solution in the presence of amine exhibits a catalytic wave before the metal-aqua complex wave. The linear dependence of the current on the pH and ligand concentration up to certain values is catalytic in nature. The decrease of catalytic peak current with increase in mercury column height also suggests that the wave is kinetically controlled. The electrocapillary curves further support that an adsorption of iron-amine complexes occur on the mercury surface. The presence of an indifferent electrolyte diminishes the peak height and this effect further confirms the catalytic behavior. The method is sensitive with the detection limit upto 0.1ppm.

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