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Mini Review

The Electrochemical Sensing of Nalbuphine Opioid Analgesic Drug by the Cyclic Voltammetric and Conductometric Titration Techniques

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Abstract

A novel reliable electrochemical sensing method was suggested for direct and sensitive determination of Nalbuphine (NB) analgesic drug. The effect of copper ions (Cu^{+2}) as sensor towards NB determination was evaluated using cyclic voltammetry method and conductometry. They have been utilized to predict the possible electrochemical sensitivity and complexation reaction between Nalbuphine Hydrochloride (NB) and divalent copper (II) metal ions. Cyclic voltammetry study of $CuSO_4.5H_2O$ in absence and presence of (NB) was performed using different concentration from Cus and NP·HCl at different scan rates. Redox mechanism of the system was determined from the resulted data. Moreover, thermodynamic parameters show valuable information about chelate metal ions. The resulted data obtained from cyclic voltammetry measurements was supported by conductometric titration measurements, since complexation of Cu (II) with (NB) has been investigated conductometric ally. The formation constants of the prepared complexes were obtained from the relation between the molar conductance and the ratio of metal to ligand concentrations indicating the formation of 1:2 and 1:1 (M: L) stoichiometric complexes. As the temperature increases, the formation constants of the complexes increase indicating that the reaction is endothermic. The negative results of ΔG indicated that the reactions between NB·HCl and Cu (II) tend to proceed spontaneously.

Keywords: Electrochemical Sensing; Nalbuphine Hydrochloride; Glassy Carbon Electrode; Cyclic Voltammetry; Stability Constant and Conductivity

Introduction

Nalbuphine, is a semisynthetic narcotic selective receptor modulators or known as mixed agonist/antagonist analgesic of the phenanthrene series [1]. Nalbuphine, structurally belongs to the strong potent opiate agonists oxymorphone and to most used opioid antagonists, naloxone and naltrexone [2]. Analytical methods such as HPLC, spectroscopy, and electrochemical techniques are influential tools for determining drug concentrations of NB in biological and pharmaceutical samples [3-5]. Detection of the complex formation reaction by cyclic voltammetry and condctometry methods confirm the potential for electrochemical sensing of Nalbuphine hydrochloride by copper ions as an electrochemical sensor.

Electrochemical sensing do not face the obstacle of high cost and complexity of setup. Cyclic voltammetry is one of the most powerful electrochemical techniques [6]. It can quickly give qualitative data about electrochemical reactions [7]. The data obtained from cyclic voltammetry investigate the behavior of electrochemical reaction. The potential and the current at which the analyte is reduced and oxidized can be obtained [8]. Stability constant and thermodynamic properties such as Gibbs free energy ΔG [9], enthalpy ΔH, and entropy ΔS [10] can be calculated where they indicate the nature of the complexation reaction [9,10].

Results and Discussion

Cyclic Voltammetry Measurements

Effect of different concentrations of Cu^{+2} and NB with different scan rates were studied as such as Effect of different scan rates. The I_p is directly proportional to $\nu^{1/2}$ which support a diffusion controlled reaction. The different solvation parameters (Γ_c, Q_c, Γ_a & Q_a) decreased by the increase of the scan rate also supporting the diffusion process of solvation. The increase of scan rate was followed by the increase of the potential difference (ΔE) but E°

value is nearly constant. Also, the redox peaks currents decreased by decreasing the scan rates. The linear relation between $-I_{pa}$ and I_{pc} with the square root of scan rate demonstrated that the reaction was governed by the surface diffusion processes [11].

The addition of NB to the solution and step wisely increasing its concentration, the redox peaks current decreased than observed with Cu^{+2} alone indicating the complex reaction between metal and ligand, hence the method is sensitive to detect NB. Also, The heterogeneous rate constant (k_s) and the kinetic parameters decreased due to the lowering of charge transfer velocity indicating more interaction between copper ions and Nalbuphine.

Effect of different scan rates in presence of Nalbuphine HCl

The influence of different scan rates for 1:1 ratio between copper and nalbuphine had been studied. The decrease of the scan rate was followed by the decrease of the redox peaks currents and the heterogeneous rate constant (k_s), but the solvation parameters like ((Γ_c, Q_c, Γ_a & (-) Q_a) increased. The linear relation between the peak current and square root of scan rate confirmed that the reaction was governed by diffusion processes.

The stability constant for (Cu-Nalbuphine) complex

The values of stability constant (Log βj) and Gibbs free energy (ΔG) increased by increasing the j (L/M) ratio, indicating the tendency towards the formation of the complex

Conductometry measurements

The specific conductance values (K_s) of the solutions of different concentrations of $CuSO_4.5H_2O$ were measured experimentally in absence and in presence of ligand at different temperatures. The molar conductance (Λ_m) values were calculated. The experimental data of (Λ_m) were analyzed for the determination of formation constants for each type of the stoichiometric complexes. The formation constants (K_f) for $CuSO_4.5H_2O$ complex were calculated for each type of complexes (1:2) and (1:1) (M: L) [12]. The obtained values of log (K_f) for the metal-ligand stoichiometric complexes are presented in for $CuSO_4.5H_2O$ in ($MeOH-H_2O$) mixture. The relation between Λ_m and the [M]/[L] molar ratio for $CuSO_4.5H_2O$ in presence of Nalbuphine HCl showed the inflections which indicate the formation of different complexes. Increasing temperature is followed by decrease in log K_f favouring less solvation for interaction of $CuSO_4.5H_2O$ with Nalbuphine HCl indicating migration of ions away from the collecting area. The Gibbs free energies of formation for 1:1 and 1:2 (M:L) stoichiometry complexes (ΔG_f°) were calculated [13].

The enthalpy (ΔHf) for the metal salt complexes were calculated for each type of complexes, (1:2) and (1:1) (M: L) by using van't Hoff equation: On plotting of log K_f versus 1/T different lines are obtained for the formation of 1:2 and 1:1 (M: L) stoichiometric complexes for $CuSO_4.5H_2O$ with Nalbuphine HCl. Formation thermodynamic parameters (ΔG_f, ΔH_f, $T\Delta S_f$, ΔS_f) were calculated Decreasing in ΔG_f° by increasing in temperatures indicating more spontaneous process.

Conclusion

In the present work, an effective glassy carbon electrode has been designed to sensing electrochemical behavior of Nalbuphine opioid analgesic drug by the cyclic voltammetry technique as well conductometric titration technique. Under optimized conditions the cyclic voltammetry results such as the electro-active surface coverage (Γ), the transfer coefficient (α), standard rate constant (Ks) and diffusion coefficient (D) were calculated. The obtained data give good analytical performance including suitable precision, excellent linear dynamic range and good detection and reproducibility. The results were obtained for different concentration of NB in mixed solvent (Methanol/ Water) with (30: 70 % V/V). We suggest that the cyclic voltammetry technique can be used as a beneficial method to be applicable in the pharmaceutical quality control laboratory and other medical applications.

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