The electrochemical effect of different temperatures on sodium saccharine in blood medium using modified working electrode CNT/GCE by cyclic voltammetry

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Abstract
Sodium Saccharin (NaSc) was studied as a chemical compound used for diabetic patients as a replacement for natural sugar. The study was focused on the effect of different temperatures on NaSc in human blood medium using cyclic voltammetric technique at modified glassy carbon electrode (GCE) with carbon nanotubes (CNT) as working electrode (CNT/GCE). The physical chemistry functions were studied for the activated values in terms of enthalpy (ΔH*), free energy (ΔG*) and entropy (ΔS*) for redox current peaks of NaSc in blood medium at both electrodes, GCE and CNT/GCE using Eyring equations. Also, the study included the determination of the activation energy (Ea*) determined by Arrhenius equations for the redox current peaks of NaSc to compare values obtained by GCE and CNT/GCE. It was found that the values of thermodynamic functions were different due to the oxidation – reduction reaction of NaSc in blood medium which reacts with many complex compound with the component of the blood especially hemoglobin as ferric and ferrous ions. The oxidative stress of NaSc in blood medium appeared clearly in voltammogram.

Keywords: sodium saccharin, nano-sensor, cyclic voltammetry, temperature, thermodynamic parameters.

1. Introduction
A recent study identified the extent of the impact of alternative chemical compounds for sugar such as sodium saccharin on blood composition in human blood samples, using electrochemical method [1]. Other studies used modified electrodes for the determination of chemical compounds in blood medium [2-8].

A new preparation of a biocompatible and conductive interface for immobilization and electrochemical detection of cells and application of carbon nanofiber in cyto-sensing was studied by cyclic voltammetry. The sensitivity of the method was good with a detection limit of 1 × 10⁻⁷ cells mL⁻¹ with cells ranging from 5 × 10⁻⁴ to 5.0 × 10⁻¹ cells mL⁻¹ [9].

The redox behavior of Cd(II) and the interaction of Cd(II) with cyclic amino acid, proline, have been studied in 0.1 M KCl, 0.1 M NaClO₄ and acetate buffer of different pH. The CVs were recorded at glassy carbon electrode within the potential window 200 and −1500 mV. The reference and counter electrode used were Ag/AgCl and Pt wire, respectively. The cyclic voltammograms showed one pair of cathodic and anodic peaks for the Cd(II)/Cd(0) system indicating the involvement of two electron transfer processes. The peak potential shift and charge transfer rate constant (kf) values indicated the interaction between metal and ligand. The higher value of peak current ratio and peak potential separation (ΔE) indicated that the systems are quasi-reversible. The effect of supporting electrolyte and concentration of electro active species on the interaction were also studied [10].

Methionine were synthesized in aqueous electrolyte with heavy metal complexes such as Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) using cyclic voltammetry. The results of the electrochemical analysis confirmed by the current potential data of peak separation (ΔE) and the peak current ratio (Ipa/Ipc) of the (Mn, Cu and Cd) complexes that the charge transfer processes are irreversible, the systems are diffusion controlled and also adsorptive controlled, and the charge transfer rate constant of metals in their complexes are less than those in their metal salts at identical experimental conditions due to the coordination of metal with methionine [11,12]. The voltammetric study of manganese complex with saccharine was studied to determine the redox current peaks of the complex as irreversible process at different pH and concentrations [13]. Linear Sweep Voltammetry and Galvanostatic Reduction techniques were used to study the oxidation of copper oxide CuO₂ using vacuum and low-pressure-based to characterization the oxidation reaction [14].
In the present paper, NaSc in blood medium was studied at different high temperatures using cyclic voltammetry to determine the thermodynamic parameters of electrochemical analysis equations.

2. Experimental

2.1. Materials
Sodium saccharin (purity 98% from Chinese company), carbon nanotubes (purity 99%) supplied from Fluka company (Germany). Healthy human blood samples were received from Iraqi Blood Bank in Baghdad City of Medicine. Deionized water was used for preparation of aqueous solutions. All solutions used in the cyclic voltammetry cell were treated with nitrogen gas for 10-15 minutes to remove the oxygen from the solutions.

2.2. Apparatus
An instrument of EZstat series (Potentiostat/Galvanostat) NuVant Systems Inc. (USA) was used in the experiments. The Electrochemical Bio-analytical cell was connected to a potentiostat device and was monitored by a special software to perform cyclic voltammetry (CV). Silver-silver chloride reference electrode (Ag/AgCl in 3M NaCl) and Platinum wire (1 mm diameter) were used as a reference and counter electrodes, respectively. The glassy carbon working electrode (GCE) modified with CNT was used in this study after cleaning with alumina solution and treated with ultrasonic path water for ten minutes.

2.3 Preparing the modification of GCE with CNT (CNT/GCE)
Mechanical attachment technical method was employed to prepare the CNT/GCE working electrode as a nano-sensor [15,16]. The method of the modification of GCE included abrasive application of multiwall carbon nanotubes (MWCNT) on the clean surface of GCE, forming an array of MWCNT as modified working electrode MWCNT/GCE and replaced in 10 ml of electrolyte in the cyclic voltammetric cell, then connected all electrodes (working electrode, reference electrode and counter electrode) with the potentiostat.

2.4 Measurements of different temperatures
A 10 ml size cell was used to measure the cyclic voltammograms. Solutions were replaced for studying at different temperatures. Three electrodes (working, reference and counter electrodes) as well as a thermometer were submerged into the cell to follow the solution temperature, and the three electrodes were connected to the potentiostat. The cell was placed into a water bath to set the required temperature and a hot plate was used to increase the temperature in the cyclic voltammetric tests.

2.5 Scanning electron microscopy (SEM) study
The SEM photographs were recorded at a magnification of 1000-6000× depending on the composition of the sample. SEM analysis was carried out to investigate microcrystals. Samples were dehydrated for 45 min before being coated with gold particles using a SEM coating unit. SEM was used to examine the morphology of CNT by mechanical attached technique on a graphite electrode surface before and after electrolysis with NaSc by cyclic voltammetry using blood medium as an electrolyte. Fig. 1.a indicates the SEM image of CNT attached onto basal plane graphite electrode for electrolysis in blood medium that exhibited an array of microcrystals with 0.1-2 μm diameter. Fig. 1.b indicates the SEM image of the modified electrode after electrolysis with NaSc using cyclic voltammetry with slightly enlarged size range of 0.1-3 μm diameter indicating presence of solid to solid conversion and that the film appears stable even after 10 potential cycling.

3. Results and discussion
3.1. Effect of varying temperature
NaSc in blood medium was studied at different temperatures using each of GCE and modified GCE with cyclic voltammetric technique to determine the physical chemistry properties in terms of activation energy and thermodynamic parameters using Arrhenius equations [17-19] and Eyring equations [20-22], respectively.

3.1.1 Activation energy (E*)
NaSc in blood medium was studied at different temperatures using GCE and CNT/GCE to determine the activation energy (E*). It was found that the cathodic current peak was enhanced
gradually at the range of temperature from 29 to 40°C. Figs 2 and 3 show the plot of $\ln(I_{pc})$ of NaSc versus reciprocal of temperature on GCE and CNT/GCE respectively, which is found to be fairly linear in agreement with thermodynamic expectation of Arrhenius equation; see Eqs (1) and (2) [17-19]. Also, the results of anodic current peaks are represented in Figs 4 and 5, illustrating the relationship between $\ln(I_{pc})$ of NaSc and reciprocal of temperature at GCE and modified working electrode CNT/GCE. The activation energy ($E_a$) values were calculated from the following Arrhenius equations:

$$\sigma = \sigma^* e^{-E_a/RT}$$  \hspace{1cm} (1) \\
$$D = D^* e^{-E_a/RT}$$  \hspace{1cm} (2)

Where

$\sigma/D$ – conductivity/diffusibility.  
$\sigma^*/D^*$ – standard conductivity/initial diffusibility.  
$E_a$ – activation energy  
$R$ – universal gas constant  
$T$ – temperature

The values of activation energy of cathodic ($E_{apc}$) and anodic ($E_{apa}$) current peaks of NaSc in blood medium at CNT/GCE are 24.98 kJ/mol.K and 33.48 kJ/mol.K respectively that can be compared with the values at GCE which is $E_{apc} = 34.45$ kJ/mol.K and $E_{apa} = 25.96$ kJ/mol.K as shown in Table 1. By comparing the activation energy values of NaSc in blood medium at GCE and CNT/GCE, it can be concluded that the value of $E_{apc}$ was declined from 34.45 at GCE to 24.98 because of using the nano-sensor of working electrode. But, in oxidation process of NaSc in blood medium the activation energy at GCE is less than that of at modified electrode CNT/GCE. It can be attributed to the viscosity of blood components which act as inhibition of the anodic conductivity [22].

### 3.1.2 Thermodynamic functions

Activation free energy ($G$), enthalpy ($H$) and entropy ($S$) of NaSc in blood medium at CNT/GCE and GCE were determined from Eyring equation, see Eq. (3) [20-22] and thermodynamic equations [23]:

$$y = -4.0273x + 15.55$$  \hspace{1cm} $R^2 = 0.9133$

$$y = -4.144x + 16.309$$  \hspace{1cm} $R^2 = 0.8382$

$$y = -3.0046x + 12.966$$  \hspace{1cm} $R^2 = 0.9026$

$$y = -4.6775x + 18.148$$  \hspace{1cm} $R^2 = 0.9306$
\[ \Delta G^* = -RT \ln \left( \frac{k \text{ h}}{T \text{k}_B} \right) \]  

(3)

\[ \Delta H^* = \Delta G^* + T \Delta S^* \]  

(4)

\[ \text{And} \ \Delta H^* = \Delta G^* + T \Delta S^* \]  

(5)

The different units are accounted for in using either the gas constant \( R \) (8.314 J/mol·K), the Boltzmann constant \( k_B \) (1.381×10−23 m²·kg·sec⁻²·K⁻¹), and Planck constant \( h \) (6.626×10−34 J·sec) as the multiplier of temperature \( T \) (K).

Table 1 illustrates the thermodynamic functions of NaSc in blood medium, the results in the table can be concluded that the spontaneous reaction was depended on more than one factors according to the law of Gibb’s free energy, not only depend on change in enthalpy (\( \Delta H^* \)) to interact and build on the Gibbs law, the reaction is becoming spontaneous when the free energy change \( \Delta G^* \) is negative and enthalpy change \( \Delta H^* \) is also negative, but entropy \( \Delta S^* \) is positive [23]. The electrochemistry reactions such as the oxidation – reduction process for NaSc compound in blood medium was studied at different temperatures to find out if the status of the reaction for the oxidation-reduction is spontaneous or nonspontaneous. Also, the working electrode affected the processes as electro-catalyst for enhancement the current in the system when using nanoparticles like CNT. In this study, the modified working electrode CNT/GCE was used to determine the functions as shown in Table 1 to study the reduction and oxidation current peaks of NaSc in blood medium which were indicated in Figs 2-5.

4. Conclusions

The effect of different working temperature on redox process of NaSc in blood medium was studied at different electrodes (GCE and CNT/GCE) in cyclic voltammetric method to determine the thermodynamic functions and activation energy using Arrhenius equations and Eyring equation. Sodium saccharine has oxidation–reduction current peaks in blood medium, so it can be considered that NaSc is an oxidative reagent in blood medium with the oxidation current peak at 750 mV. Activation energy values were determined from Arrhenius equations at both GCE and CNT/GCE electrodes for both cathodic and anodic peaks; nanoparticles made activation energy values to be reduced in blood medium. Activation of free energy (G), enthalpy (H) and entropy (S) of NaSc in blood medium can be calculated from Eyring equation and other thermodynamic equations. The same values were found for each electrodes (GCE and CNT/GCE), so the values of thermodynamic functions are not effected by the electrode, but the spontaneous oxidation-reduction reaction depended on these functions.

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Hőmérséklet hatása nátrium szacharinátra vér közegben ciklikus voltammetria vizsgálatok során CNT/GCE elektródával mért

A hőmérséklet elektrokémiai hatása nátrium szacharinátra vár közegben ciklikus voltammetria vizsgálatok során CNT/GCE elektrodával mérvé

A cikk bemutatja a hőmérséklet hatását nátrium szacharinátra emberi vér közegben ciklikus voltammetria vizsgálatok során. A mérések szén nanocsövekkel (CNT) módosított üvegszerű szén elektrodával (GCE) végzették. A fizikai kémiai paramétereket (entalpia, szabad energia és entrópia) az Eyring egyenletekből határozták meg a redox áramcsúcsok mérséi eredményei alapján. Az aktiválási energia mértékét az Arrhenius egyenlete alapján, elsősorban a vér vasion tartalmú hemoglobinjával.

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