

Article

Interfacial Activation and Electronic Coupling at Platinum Electrodes Induced by Vitamin B6 and Silver Nanoparticles in Sulfate Electrolyte: A CV-EIS-UV-Vis Study

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Abstract

This study establishes a unified electrochemical–optical framework to elucidate adsorption-controlled charge transfer and electronic excitation at platinum–electrolyte interfaces modified by biomolecules and metal nanoparticles. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and UV-Vis absorption spectroscopy with Tauc analysis were used to probe transformations induced by vitamin B6 (pyridoxine) and silver nanoparticles (nAg) in Na₂SO₄ aqueous electrolytes. In the supporting electrolyte, platinum behaves as a blocking capacitive interface with nearly symmetric anodic–cathodic charges, high charge-transfer resistance ($R_{ct} \approx 3.14 \text{ k}\Omega\cdot\text{cm}^2$), low double-layer capacitance ($C_{dl} \approx 4.0 \times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$), and deep-UV transitions ($E_{low} \geq 3.8 \text{ eV}$), confirming the electrochemical inertness of sulfate media. Vitamin B6 molecules interact with the electrode surface and modify the structure of the electrical double layer at the platinum/electrolyte interface, restructuring the double layer, increasing C_{dl} ($\approx 1.2 \times 10^{-4} \text{ F}\cdot\text{cm}^{-2}$), decreasing R_{ct} ($\approx 0.23 \text{ k}\Omega\cdot\text{cm}^2$), and generating irreversible surface-confined anodic processes. Tauc plots yield two transitions ($E_{low} \approx 2.9 \text{ eV}$; $E_{high} \approx 4.1 \text{ eV}$), attributed to molecular states and weak charge-transfer interactions. The results suggest electronic interactions between the silver nanoparticles and the adsorbed vitamin B6 molecules at the electrode interface. Strong electronic interactions between vitamin B6 and nAg yields ultralow R_{ct} ($\approx 58 \text{ }\Omega\cdot\text{cm}^2$), enhanced pseudocapacitance ($C_{dl} \approx 2.9 \times 10^{-4} \text{ F}\cdot\text{cm}^{-2}$), and red-shifted transitions ($E_{low} \approx 2.2 \text{ eV}$; $E_{high} \approx 3.7 \text{ eV}$). These results show that adsorption-induced electronic coupling governs interfacial kinetics and optical excitation pathways.

Keywords: vitamin B6; sulphate; EIS; electric double layer; UV-Vis optical transition energies

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1. Introduction

Vitamin B6 comprises a structurally diverse family of water-soluble vitamers, including pyridoxine, pyridoxal, pyridoxamine, and their phosphorylated derivatives, which are essential cofactors in amino acid metabolism, neurotransmitter synthesis, immune regulation, and erythropoiesis [1–5]. Since its identification and structural elucidation in the early twentieth century, vitamin B6 has been recognized as a universal metabolic regulator involved in more than one hundred enzymatic reactions across biological systems [1,5]. Insufficient vitamin B6 levels are associated with anemia, neuro-

logical impairment, immune dysfunction, and metabolic imbalance, whereas adequate intake is increasingly linked to protection against oxidative stress, inflammation, and age-related diseases [3–5].

Beyond its biochemical significance, vitamin B6 exhibits complex redox and photochemical behavior that is strongly dependent on molecular structure, protonation state, and local environment [1,6]. Under ultraviolet irradiation, B6 vitamers can act as endogenous photosensitizers, generating reactive oxygen species, while under other conditions, they behave as efficient antioxidants and radical scavengers [1]. This dual oxidative–protective character makes vitamin B6 particularly relevant in electrochemical and photochemical systems where adsorption, charge transfer, and solvation phenomena are closely coupled [1,6,7].

Accurate determination of vitamin B6 is essential in pharmaceutical quality control, food analysis, fermentation monitoring, and clinical diagnostics [3,8–14]. Although conventional techniques such as spectrophotometry, chromatography, electrophoresis, and mass spectrometry provide high sensitivity and selectivity, they often require complex instrumentation, extensive sample preparation, and long analysis times [5,8–10,15]. These limitations have driven increasing interest in alternative analytical approaches that are faster, simpler, and compatible with in situ measurements [4,11].

Electrochemical methods have emerged as particularly attractive tools for vitamin B6 detection due to their sensitivity, cost efficiency, rapid response, and suitability for miniaturized platforms [4,11,13]. Numerous studies have shown that vitamin B6 undergoes predominantly irreversible or quasi-irreversible oxidation at solid electrodes, enabling its electroanalytical determination [7,14,16]. Screen-printed electrodes, potentiometric sensors, and ion-selective membranes have been successfully applied to vitamin B6 quantification in pharmaceutical and food samples, offering low detection limits and good selectivity [16–18].

Fundamental electrochemical studies indicate that vitamin B6 oxidation is strongly surface-dependent and often governed by adsorption-controlled EC or ECE mechanisms [6,7]. Electrode material, surface chemistry, and crystallography play decisive roles in determining electron-transfer kinetics and reaction pathways [6,7,19]. Boron-doped diamond electrodes, for example, offer wide potential windows and low background currents, enabling reliable detection of vitamin B6 in complex biological matrices [14,19]. To overcome kinetic limitations and enhance analytical performance, extensive efforts have focused on electrode modification using nanostructured materials and hybrid architectures [12,20–23]. Nanoporous metals, carbon-based composites, metal oxides, and redox-active polymers increase electroactive surface area, promote vitamin adsorption, and accelerate electron transfer [12,20–22]. Among these strategies, metallic nanoparticles play a central role by introducing highly conductive nano-domains and facilitating electronic coupling between adsorbed biomolecules and the underlying electrode [23,24]. Gold- and silver-based nanostructures have been shown to lower oxidation overpotentials, enhance peak currents, and stabilize reactive intermediates, often accompanied by electric double-layer restructuring and pseudocapacitive behavior [10,24–26].

Electrochemical impedance spectroscopy provides a powerful framework for resolving these interfacial effects by separating resistive, capacitive, and kinetic contributions over broad frequency ranges [21,24,25]. EIS studies have demonstrated that vitamin B6 adsorption, ion pairing, and nanoparticle incorporation significantly affect charge-transfer resistance, interfacial time constants, and double-layer capacitance, frequently requiring constant phase elements to account for interfacial heterogeneity [21,25].

Metallic nanoparticles, particularly silver nanoparticles, have attracted extensive attention due to their unique electronic, optical, and catalytic properties, which differ

fundamentally from bulk materials [27–29]. Advances in green and biogenic synthesis routes using plant extracts, polysaccharides, proteins, polyphenols, and vitamins have enabled precise control over nanoparticle size, morphology, and surface chemistry while reducing environmental impact [27,29,30]. The optical properties of silver nanoparticles, especially their surface plasmon resonance, are highly sensitive to particle size, aggregation state, and local dielectric environment, making UV-Vis spectroscopy a key tool for probing nanoparticle–molecule interactions and electronic coupling [28,29,31].

Silver nanoparticles are widely integrated into electrochemical systems, where they act as conductive bridges, electron reservoirs, and catalytic centers that promote charge transfer and surface redox reactions [23,28]. Their biological activity and toxicity strongly depend on physicochemical parameters such as size, surface functionalization, and Ag⁺ release, with green synthesis and biomolecule-mediated stabilization significantly mitigating adverse effects [29,30,32–34]. From an electrochemical perspective, the same interfacial phenomena governing biological activity—adsorption, surface coordination, local electric-field modulation, and controlled ion release—also dictate the behavior of nAg-modified electrodes [23,24]. Electrochemical synthesis and immobilization strategies, including in situ formation of nAg on conductive substrates or within polymeric and multilayer matrices, have further demonstrated that silver nanoparticles can be stabilized directly at electrode interfaces while retaining high electrochemical activity and controlled interfacial architecture [35].

The interfacial design principles emerging from nanoparticle-modified electrochemical systems underscore the central role of engineered charge-transfer landscapes, adsorption energetics, and local electronic structure in governing complex multi-electron reactions. These concepts are equally relevant in modern electrocatalytic contexts such as nitrate reduction to ammonia (e-NO₃RR), where coupled proton–electron transfer steps and intermediate stabilization are dictated by finely tuned interfacial environments. More broadly, similar strategies are increasingly being translated into low-dimensional and heterostructured material platforms, where controlled band alignment, interlayer coupling, and defect engineering provide additional degrees of freedom to modulate catalytic and electrochemical activity across diverse energy conversion and sensing applications [36,37].

Vitamin molecules can act simultaneously as nanoparticle stabilizers and redox-active species, a dual functionality that is particularly relevant for vitamin B6 due to its multiple polar functional groups capable of coordinating silver surfaces while participating in surface-confined redox processes [7,27,31]. Consequently, integrating silver nanoparticles into vitamin B6-modified electrochemical interfaces represents a rational strategy for engineering highly electroactive, pseudocapacitive systems with enhanced charge-transfer kinetics and dynamic interfacial response [23,24,34].

Although previous studies have investigated either the electrochemistry of vitamin B6 or the electrocatalytic effects of Ag nanoparticle-modified electrodes separately [6,7,10,14,21,23–26], a systematic correlation between cyclic voltammetry, electrochemical impedance spectroscopy, and optical (UV-Vis/Tauc) characterization for Pt|Na₂SO₄|vitamin B6 interfaces containing silver nanoparticles has not yet been reported. In the present work, we investigate the interfacial electrochemistry of vitamin B6 at platinum electrodes in aqueous electrolytes, with emphasis on the role of silver nanoparticles in modulating adsorption, electric double-layer structure, and charge-transfer dynamics. By combining cyclic voltammetry, electrochemical impedance spectroscopy, and UV-Vis spectroscopy, we demonstrate how nanoparticle–biomolecule coupling transforms a partially blocking, adsorption-dominated interface into a highly electroactive, pseudocapacitive hybrid system, providing fundamental insight relevant to advanced electrochemical sensors and functional noble-metal interfaces.

2. Materials and Methods

2.1. Chemicals and Solutions

All chemicals were of analytical grade and used as received without further purification. Sodium sulfate (Na_2SO_4 , $\geq 99.0\%$, Merck, Darmstadt, Germany) and vitamin B6 (pyridoxine hydrochloride, $\geq 99.0\%$, purchased from a local pharmacy) were purchased from commercial suppliers and used as supporting electrolyte and electroactive biomolecule, respectively. Silver nanoparticles (nAg, aqueous dispersion, Aghoras Invent srl, Bucharest, Romania) were used as received. The silver nanoparticles were used as received from the supplier without additional physicochemical characterization. The dispersions were freshly prepared before each electrochemical experiment and homogenized immediately prior to use in order to minimize sedimentation. The electrochemical measurements were completed within a time interval during which no visible precipitation or macroscopic aggregation was observed. Therefore, the results are interpreted as the electrochemical response of the nanoparticle dispersion under the employed experimental conditions rather than as a function of nanoparticle size distribution or colloidal stability.

Aqueous electrolyte solutions were prepared using distilled water. The supporting electrolyte consisted of 0.1 M Na_2SO_4 . Vitamin B6 was added to obtain a final concentration of $0.05 \text{ g}\cdot\text{L}^{-1}$. A single concentration of vitamin B6 ($0.05 \text{ g}\cdot\text{L}^{-1}$) was used in this study in order to investigate its effect on the interfacial electrochemical behavior of the platinum electrode under controlled conditions. The concentration of vitamin B6 was selected to ensure measurable interfacial electrochemical effects while also providing suitable absorbance values for the UV-Vis measurements, enabling reliable application of the Beer-Lambert Law in the subsequent optical analysis. The aim of this work was not the development of a concentration-dependent electrochemical sensor, but rather the investigation of interfacial processes induced by vitamin B6 adsorption and their interaction with silver nanoparticles. For hybrid systems, silver nanoparticles were introduced at a concentration of $70 \text{ mg}\cdot\text{L}^{-1}$. The concentration of silver nanoparticles was selected to ensure stable dispersion in the electrolyte and to produce measurable interfacial effects while avoiding excessive aggregation of the nanoparticles. This concentration was also compatible with the UV-Vis spectroscopic measurements performed for optical characterization of the hybrid system. All solutions were freshly prepared prior to each experiment and deaerated by nitrogen bubbling for at least 15 min before electrochemical measurements.

2.2. Electrochemical Cell and Instrumentation

Electrochemical experiments were carried out in a conventional three-electrode glass cell connected to a computer-controlled potentiostat/galvanostat VoltaLab 40 (Radiometer Analytical SAS, Lyon, France, VoltaMaster 4 software, version 7.8.26338.3). A platinum electrode (geometric area = 1.0 cm^2) served as the working electrode. A platinum wire was used as the counter electrode, and an Ag/AgCl (sat KCl) electrode was employed as the reference electrode. All potentials reported in this work are referred to the Ag/AgCl reference electrode.

Prior to each experiment, the platinum working electrode was mechanically polished using alumina suspensions of decreasing particle size (1.0, 0.3, and $0.05 \mu\text{m}$), thoroughly rinsed with deionized water, and sonicated in ethanol and water for 5 min each to remove residual contaminants. The electrode was then electrochemically cleaned by cycling in 0.5 M H_2SO_4 between -0.2 and $+1.2 \text{ V}$ until a stable voltammetric response characteristic of a clean platinum surface was obtained.

All measurements were performed at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$).

2.3. Cyclic Voltammetry

Cyclic voltammetry (CV) was performed in the potential window from -1.5 V to $+2.0$ V at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$, unless otherwise stated. The anodic and cathodic charges were calculated by numerical integration of the current-potential curves according to: $Q = 1/\nu \int I(E) dE$ where $I(E)$ is the current density as a function of the applied potential E and ν is the potential scan rate ($\text{V}\cdot\text{s}^{-1}$). Anodic and cathodic charges were obtained by integrating the positive and negative current branches, respectively, and are reported in coulombs per square centimeter ($\text{C}\cdot\text{cm}^{-2}$).

2.4. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were carried out at the open-circuit potential with a sinusoidal perturbation amplitude of 10 mV over a frequency range from 100 kHz to 0.1 Hz . Impedance spectra were recorded after stabilizing the electrode for at least 10 min in each electrolyte. The impedance data were analyzed using Nyquist and Bode representations and fitted to appropriate equivalent circuit models using complex nonlinear least-squares fitting software. The solution resistance (R_s), charge-transfer resistance (R_{ct}), constant phase element (CPE) parameters, and apparent double-layer capacitance (C_{dl}) were extracted from the fitted models. The double-layer capacitance was estimated from the characteristic frequency f_{max} corresponding to the maximum of the imaginary impedance according to: $C_{dl} = 1/(2\pi R_{ct} f_{max})$. All impedance parameters are reported as area-normalized values ($\Omega\cdot\text{cm}^2$, $\text{F}\cdot\text{cm}^{-2}$).

2.5. UV-Vis Spectroscopy and Tauc Analysis

UV-Vis absorption spectra of the electrolyte solutions were recorded using a double-beam spectrophotometer (model Varyan Cary 50 UV-Vis spectrophotometer, Varian Inc., Mulgrave, VIC, Australia with CaryWin UV software, version 3) in quartz cuvettes with an optical path length of 1 cm over the wavelength range $200\text{--}800 \text{ nm}$.

The absorption coefficient α was calculated from the measured absorbance, and the apparent optical transition energies were estimated using the Tauc formalism: $(\alpha h\nu)^n = A(h\nu - E_{opt})$ assuming direct allowed transitions ($n = 2$). Two characteristic transition energies were extracted: (i) E_{low} obtained from the low-energy linear region near the absorption onset, and (ii) E_{high} , obtained from the higher-energy linear region associated with intrinsic molecular or hybrid electronic transitions. The application of the Tauc formalism in the present study is intended as a phenomenological approach for estimating characteristic optical transition energies rather than true electronic band gaps in the solid-state sense. Although Tauc analysis was originally developed for bulk semiconductors, here it is applied as a phenomenological tool to estimate effective optical transition energies in the Pt|vitamin B6|nAg interfacial system, enabling comparison of E_{low} and E_{high} shifts induced by molecular adsorption and metal–organic electronic coupling, rather than representing true solid-state band gaps.

3. Results and Discussion

3.1. Cyclic Voltammetric Response of Platinum in Na_2SO_4 -Based Electrolytes Containing Vitamin B6 and Silver Nanoparticles

The cyclic voltammograms (CVs) recorded at a platinum electrode in (i) 0.1 M Na_2SO_4 , (ii) 0.1 M Na_2SO_4 containing vitamin B6 ($0.05 \text{ g}\cdot\text{L}^{-1}$), and (iii) 0.1 M Na_2SO_4 containing vitamin B6 ($0.05 \text{ g}\cdot\text{L}^{-1}$) and silver nanoparticles (nAg, $70 \text{ mg}\cdot\text{L}^{-1}$) reveal substantial differences in both current magnitude and voltammetric profile (Figure 1). These differences reflect progressive changes in interfacial chemistry arising from molecular adsorp-

tion, electrochemical double-layer (EDL) restructuring, nanoparticle-mediated electronic coupling, and enhanced faradaic activity.

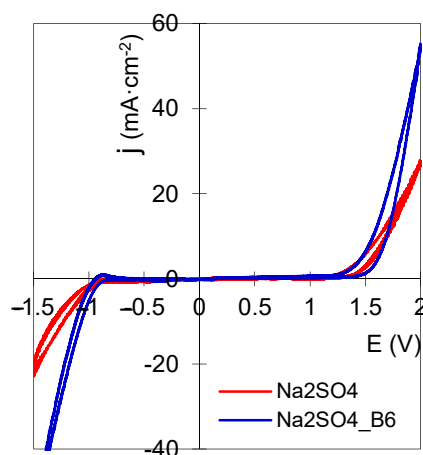


Figure 1. The cyclic voltammograms (CVs) recorded at a platinum electrode in (i) 0.1 M Na₂SO₄, (ii) 0.1 M Na₂SO₄ containing vitamin B6 (0.05 g·L⁻¹), and (iii) 0.1 M Na₂SO₄ containing vitamin B6 (0.05 g·L⁻¹) and silver nanoparticles (nAg, 70 mg·L⁻¹) reveal substantial differences in both current magnitude and voltammetric profile. These differences reflect progressive changes in interfacial chemistry arising from molecular adsorption, electrochemical double-layer (EDL) restructuring, nanoparticle-mediated electronic coupling, and enhanced faradaic activity; scan rate of 50 mV·s⁻¹.

In the absence of vitamin B6, the CV obtained in 0.1 M Na₂SO₄ exhibits the characteristic response of platinum in an electrochemically inert supporting electrolyte. The voltammetric response is dominated by broad current contributions without well-defined faradaic peaks over most of the investigated potential window, consistent with predominantly non-faradaic behavior associated with double-layer charging. The electrochemical response observed in the cyclic voltammograms is consistent with a combination of double-layer charging processes and surface reactions typically reported for platinum electrodes, including possible platinum oxide formation at positive potentials. These assignments are based on the characteristic voltammetric behavior of platinum reported in the literature and should be considered plausible interpretations rather than definitive mechanistic identification. At the highest anodic potentials explored, the contribution of oxygen evolution cannot be excluded and may partially overlap with platinum surface oxidation processes.

At negative potentials, the gradual increase in cathodic current is associated with hydrogen adsorption and the onset of the hydrogen evolution reaction (HER), whereas at positive potentials the anodic current increase corresponds to platinum surface oxidation through the formation of Pt-OH and Pt-O species [2,3]. These surface-confined processes are largely reversible, as evidenced by the modest hysteresis between forward and reverse scans [11]. The absence of distinct redox peaks confirms that Na₂SO₄ acts primarily as a supporting electrolyte, providing ionic conductivity without participating directly in faradaic charge-transfer reactions. Sulfate ions may exhibit specific adsorption on platinum and contribute to the structure of the electrical double layer; however, since Na₂SO₄ was used in all investigated systems, sulfate-related effects are expected to remain essentially constant throughout this study.

The introduction of vitamin B6 leads to pronounced changes in the voltammetric response, indicating the occurrence of both specific adsorption phenomena and faradaic reactions at the Pt|electrolyte interface (Figure 1). Vitamin B6 (pyridoxine) contains multiple polar and redox-active functional groups, including hydroxyl, amine, and het-

eroaromatic pyridine moieties, which promote strong interactions with platinum through chemisorption and electrostatic interactions [2,3,6,7].

The observed increase in capacitance, together with the decrease in R_{ct} and the appearance of irreversible anodic processes, is consistent with adsorption-mediated modification in the electrical double layer. As a consequence, the non-faradaic region exhibits enhanced capacitive currents and deviations from ideal capacitive behavior, indicating increased double-layer capacitance and interfacial heterogeneity. Although the electrochemical response clearly demonstrates adsorption-induced modification in the interface, the present data do not allow for an unambiguous distinction between specific adsorption within the inner Helmholtz plane and outer-sphere electrostatic interactions.

Superimposed on the capacitive background, additional anodic current contributions emerge that are absent in the blank electrolyte. These features are attributed to the electrooxidation of adsorbed vitamin B6 molecules, likely involving electron transfer from hydroxylated carbon centers and the pyridine ring, leading to oxidized aldehydic or quinonoid-type intermediates [1,2,6,7]. The broad and poorly resolved nature of these anodic responses suggests that vitamin B6 oxidation is adsorption-controlled rather than diffusion-limited and may be coupled to adsorption-desorption equilibria. The absence of well-defined cathodic counterparts during the reverse scan indicates that the oxidation process is largely irreversible or quasi-irreversible, involving either chemical follow-up reactions or strong retention of oxidation products on the platinum surface.

At negative potentials, adsorbed vitamin B6 partially blocks active platinum sites, attenuating hydrogen adsorption and HER kinetics. Consequently, the Pt|Na₂SO₄ + B6 interface behaves as a mixed non-faradaic/faradaic system in which capacitive EDL charging coexists with irreversible surface-confined oxidation processes. The overall electrochemical response therefore evolves from the nearly ideal capacitive behavior observed in Na₂SO₄ toward an adsorption-dominated interface characterized by enhanced anodic charge consumption and reduced electrochemical reversibility.

A further and more dramatic transformation occurs after the introduction of silver nanoparticles into the Na₂SO₄-vitamin B6 electrolyte. The CV recorded in the presence of nAg displays a substantial increase in both anodic and cathodic currents, accompanied by improved current symmetry and enhanced reversibility (Figure 1) [22–24]. These changes provide clear evidence that silver nanoparticles actively participate in interfacial charge-transfer processes and significantly modify the physicochemical properties of the electrode/electrolyte interface.

Silver nanoparticles introduce highly conductive nanodomains that increase the effective electroactive surface area and facilitate electron transport between adsorbed vitamin B6 molecules and the platinum substrate [6,7,26]. In addition, nAg can act as an electronic mediator, lowering the activation barrier for electron transfer and promoting faster interfacial kinetics.

Although the present study was not designed to investigate colloidal stability, the reproducibility of both the CV and EIS responses over independent measurements suggests that no significant sedimentation or irreversible nanoparticle deposition occurred during the electrochemical experiments. Nevertheless, complementary characterization by dynamic light scattering (DLS), zeta potential measurements, or electron microscopy would provide valuable information regarding nanoparticle stability in sulfate-containing electrolytes and should be considered in future studies.

From an EDL perspective, the presence of nAg profoundly restructures the interfacial region [27–29]. Vitamin B6 molecules can adsorb not only on platinum but also on silver nanoparticle surfaces through coordination involving hydroxyl and nitrogen-containing functional groups. As a result, a hybrid interfacial architecture consisting of Pt-B6, Ag-B6, and Pt-Ag electronic junctions is formed. This interfacial layer is more

polarizable and electronically heterogeneous than that formed in the absence of nanoparticles, leading to significantly enhanced capacitive currents.

In the non-faradaic potential region, the $\text{Na}_2\text{SO}_4 + \text{B6} + \text{nAg}$ system exhibits a pronounced increase in current relative to the B6-only electrolyte. This enhancement reflects both increased double-layer capacitance and pseudocapacitive contributions associated with rapid reversible surface redox processes involving adsorbed vitamin B6 species and silver nanoparticles [4,11].

In the faradaic region, anodic currents become markedly amplified and broadened, indicating more efficient electrooxidation of vitamin B6. The presence of silver nanoparticles facilitates electron delocalization and stabilizes intermediate oxidation states of B6, thereby enabling partial charge recovery during the cathodic sweep. This behavior is consistent with the experimentally observed increase in current symmetry and cathodic charge.

Additional contributions may arise from oxidation of Ag^0 to Ag^+ at high anodic potentials, formation of electroactive Ag-B6 surface complexes, and synergistic coupling between platinum oxide formation and silver-mediated oxidation of vitamin B6. Collectively, these processes broaden the faradaic window and generate a highly dynamic interface in which classical distinctions between capacitive and faradaic charge storage become less pronounced.

The interaction between vitamin B6 and silver nanoparticles appears to be central to the observed enhancement in electrochemical activity. Vitamin B6 may function simultaneously as a surface ligand and a redox-active molecule, stabilizing nAg dispersions while participating directly in electron-transfer reactions. Adsorption of B6 on nAg surfaces increases the residence time of electroactive species near the interface and promotes surface-confined redox cycling. Furthermore, silver nanoparticles may catalyze vitamin B6 oxidation by providing alternative reaction pathways or facilitating electron hopping between neighboring adsorption sites. These synergistic effects explain the substantial increase in current density and improved charge reversibility observed in comparison with the $\text{Na}_2\text{SO}_4 + \text{B6}$ system.

The anodic and cathodic charges were determined by numerical integration of the voltammetric curves according to:

$$Q_a = \frac{1}{v} \int_{E_{min}}^{E_{max}} I(E) dE \quad \text{for } I(E) > 0$$

$$Q_c = \frac{1}{v} \int_{E_{max}}^{E_{min}} I(E) dE \quad \text{for } I(E) < 0$$

where $I(E)$ is the current density as a function of the applied potential E , and v is the potential scan rate ($\text{V}\cdot\text{s}^{-1}$). The resulting charges are expressed in coulombs per unit area ($\text{C}\cdot\text{cm}^{-2}$).

It should be emphasized that the integrated anodic and cathodic charges (Table 1) represent the total voltammetric charge and therefore include contributions from both faradaic reactions and non-faradaic double-layer charging. Because adsorption of vitamin B6 and the incorporation of silver nanoparticles modify the interfacial capacitance, the integrated charge alone does not permit quantitative separation of capacitive and faradaic contributions. Consequently, the charge analysis is interpreted comparatively among the investigated systems and in conjunction with the electrochemical impedance spectroscopy results, which independently quantify changes in the apparent double-layer capacitance (C_{dl}) and apparent charge-transfer resistance (R_{ct}).

Table 1. Anodic and cathodic charges derived from cyclic voltammetry.

System	+ Q_{anodic} (C)	− Q_{cathodic} (C)
Na ₂ SO ₄	0.0284	0.0307
Na ₂ SO ₄ + B6	0.0878	0.0411
Na ₂ SO ₄ + B6 + nAg	0.1121	0.0988

The charges were obtained by integrating the current-potential curves according to $Q = 1/v \int I(E) dE$, where v is the scan rate (50 mV·s^{−1}).

The integrated anodic and cathodic charges provide comparative information on the evolution of the overall interfacial electrochemical response, reflecting the combined influence of charge-transfer reactions and double-layer charging. Their interpretation therefore relies on correlation with the EIS-derived kinetic and capacitive parameters. In Na₂SO₄, anodic and cathodic charges are nearly identical ($Q_a \approx |Q_c|$), indicating a predominantly reversible electrochemical response governed by double-layer charging and reversible platinum surface processes. The close charge balance confirms that charge injected during the anodic scan is largely recovered during the cathodic sweep.

The addition of vitamin B6 results in a marked increase in anodic charge ($Q_a = 0.0878$ C), while the cathodic charge increases only modestly ($|Q_c| = 0.0411$ C). Consequently, the Q_a/Q_c ratio increases significantly above unity (Table 1), providing strong evidence for irreversible or weakly reversible oxidation processes associated with adsorbed vitamin B6 molecules. The excess anodic charge is consistent with an increased contribution of adsorption-controlled oxidation reactions, although part of the increase also originates from the enhanced interfacial capacitance associated with adsorption. The interface therefore evolves toward a partially blocking, adsorption-dominated electrochemical regime.

The introduction of silver nanoparticles fundamentally alters this behavior. Although both anodic and cathodic charges increase relative to the B6-only system, the increase in cathodic charge is disproportionately larger, yielding a Q_a/Q_c ratio much closer to unity. This shift demonstrates that nAg significantly enhances charge recoverability and electrochemical reversibility. The larger cathodic charge is consistent with both enhanced charge recovery through reversible electrochemical processes and increased capacitive charge storage resulting from the larger apparent double-layer capacitance.

Several synergistic mechanisms likely contribute to this behavior: (i) pseudocapacitive charge storage associated with fast Ag/Ag⁺ and surface-confined B6 redox processes; (ii) electronic mediation by silver nanoparticles, which facilitates electron transfer during both forward and reverse scans; (iii) formation of hybrid Pt-Ag-B6 interfacial structures that stabilize intermediate oxidation states and suppress surface poisoning; and (iv) enhancement in double-layer capacitance, increasing the proportion of electrostatically stored charge.

From a mechanistic perspective, the systematic evolution of the Q_a/Q_c ratio provides a concise descriptor of interfacial transformation: a nearly ideal capacitive interface in Na₂SO₄, an adsorption-controlled and largely irreversible electrochemical regime in Na₂SO₄ + B6, and a nanoparticle-mediated pseudocapacitive interface exhibiting substantially improved reversibility in Na₂SO₄ + B6 + nAg (Table 1). These findings demonstrate that silver nanoparticles do not merely increase current through surface-area effects but fundamentally modify the charge-storage and charge-transfer mechanisms operating at the platinum interface.

Overall, the voltammetric data reveal a progressive transition from a relatively inert platinum surface in Na₂SO₄, to an adsorption-dominated and partially irreversible interface in the presence of vitamin B6, and finally to a highly electroactive and kinetically enhanced Pt-B6-nAg system. The results highlight the critical role of nanoparticle–biomolecule interactions in regulating faradaic and non-faradaic processes and under-

score the potential of platinum–organic–nanoparticle architectures for advanced electrochemical sensing, biointerfacial engineering, and hybrid catalytic applications.

3.2. Electrochemical Impedance Spectroscopy Analysis of Platinum in Na_2SO_4 -Based Electrolytes Containing Vitamin B6 and Silver Nanoparticles

Electrochemical impedance spectroscopy (EIS) measurements were performed at the open-circuit potential (OCP) in order to investigate the interfacial properties of platinum electrodes under near-equilibrium conditions. The measured OCP values were 0.261 V in 0.1 M Na_2SO_4 , 0.314 V in 0.1 M Na_2SO_4 + vitamin B6 ($0.05 \text{ g}\cdot\text{L}^{-1}$), and 0.332 V in 0.1 M Na_2SO_4 + vitamin B6 ($0.05 \text{ g}\cdot\text{L}^{-1}$) + silver nanoparticles (nAg, $70 \text{ mg}\cdot\text{L}^{-1}$) versus Ag/AgCl. Although these potentials lie predominantly within the non-faradaic region, adsorption of vitamin B6 and the presence of silver nanoparticles induce significant modifications in the electrode/electrolyte interface, allowing for meaningful estimation of apparent charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}) from impedance measurements.

The impedance spectra were analyzed using Nyquist and Bode representations to elucidate the influence of vitamin B6 and silver nanoparticles on interfacial charge transfer, electrical double-layer (EDL) structure, adsorption phenomena, and pseudocapacitive behavior [11]. Owing to the non-ideal nature of the investigated interfaces, the impedance data were fitted using a modified Randles equivalent circuit consisting of the solution resistance (R_s) connected in series with a parallel combination of the apparent charge-transfer resistance (R_{ct}) and a constant phase element (CPE), i.e., $R_s - (R_{\text{ct}} \parallel \text{CPE})$. No Warburg diffusion element was included in the equivalent circuit because none of the investigated impedance spectra exhibited the characteristic low-frequency 45° diffusion tail. The Nyquist plots are dominated by depressed semicircles over the entire measured frequency range, indicating that the impedance response is governed primarily by interfacial charge-transfer and adsorption processes rather than semi-infinite diffusion. Accordingly, the fitted R_{ct} values should be interpreted as apparent interfacial resistances describing the overall electrode/electrolyte response under the investigated conditions. The replacement of an ideal capacitor by a CPE accounts for frequency dispersion arising from surface heterogeneity, adsorption processes, distributed relaxation times, and nanoparticle-induced roughness [38,39]. The fitted CPE exponent (n) progressively decreased from the supporting electrolyte to the vitamin B6-containing and nAg-containing systems, indicating an increasing deviation from ideal capacitive behavior caused by adsorption-induced heterogeneity and nanoparticle-induced surface roughness. The high n value obtained for Na_2SO_4 approaches ideal capacitive behavior, whereas lower n values observed after addition of vitamin B6 and nAg confirm the development of increasingly heterogeneous interfacial environments. The fitted CPE exponent progressively decreased from 0.95 for the supporting electrolyte to 0.88 after addition of vitamin B6 and further to 0.82 in the presence of silver nanoparticles. This systematic decrease indicates increasing interfacial heterogeneity and progressively stronger deviation from ideal capacitive behavior, consistent with adsorption of vitamin B6 and nanoparticle-induced surface roughness.

For the supporting electrolyte alone, the Nyquist plot exhibits a well-defined depressed semicircle with a small high-frequency intercept and a large diameter (Figure 2). The high-frequency intercept corresponds to the uncompensated solution resistance ($R_s \approx 1.9 \Omega\cdot\text{cm}^2$), reflecting the high ionic conductivity of the Na_2SO_4 electrolyte. The large semicircle diameter yields an apparent charge-transfer resistance of $R_{\text{ct}} \approx 3144 \Omega\cdot\text{cm}^2$ (Table 2), indicating slow interfacial kinetics and a predominantly blocking behavior. These fitted R_{ct} values should be interpreted as effective interfacial resistances reflecting the combined contribution of double-layer charging and minor surface processes rather than purely faradaic electron-transfer kinetics.

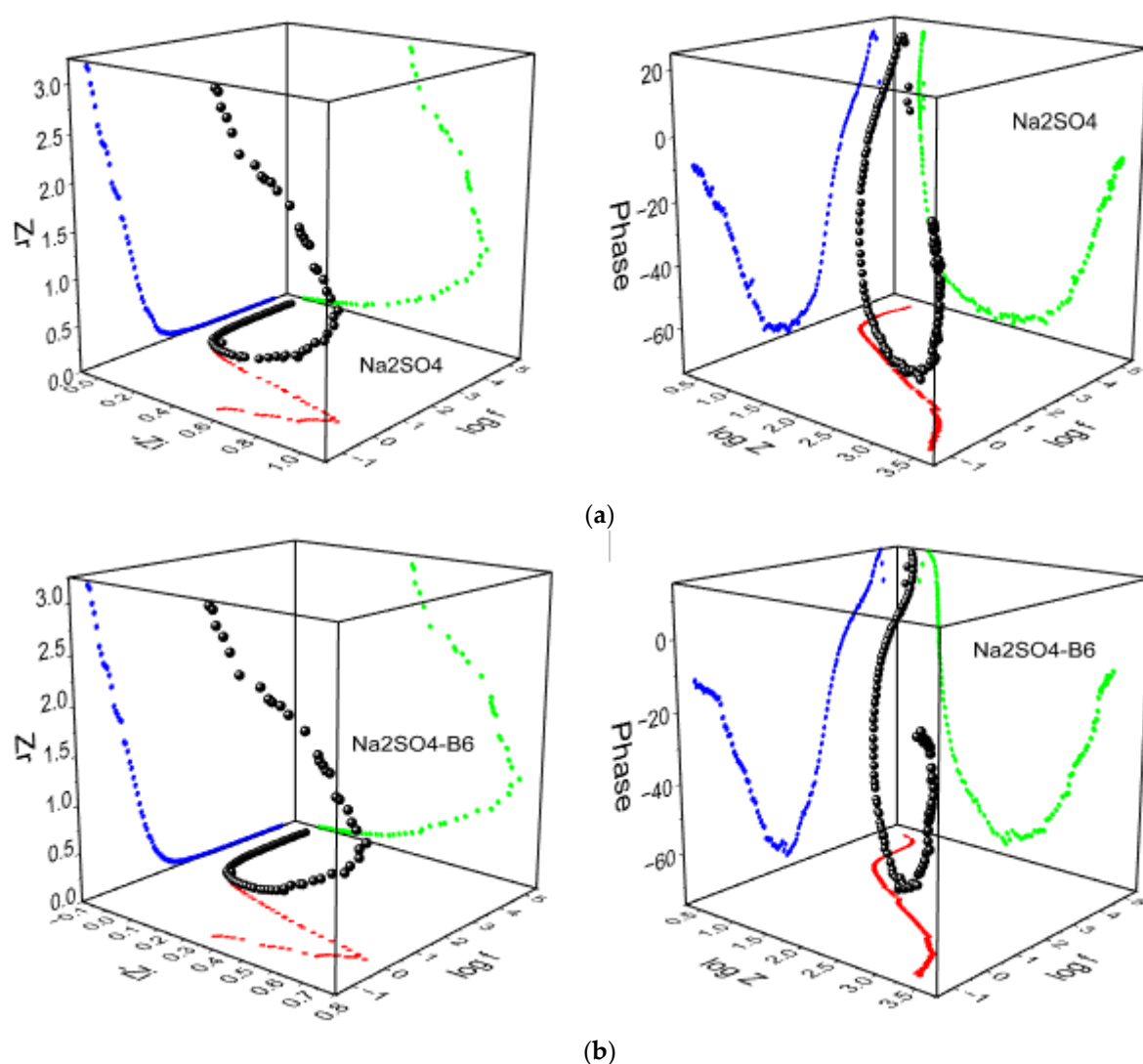


Figure 2. Three-dimensional electrochemical impedance spectroscopy (EIS) representations of a platinum working electrode (geometric area = 1 cm²) immersed in (a) 0.1 M Na₂SO₄ and (b) 0.1 M Na₂SO₄ containing vitamin B6 (0.05 g·L⁻¹). Panels include Nyquist-type representations (Z_r versus $-Z_i$ as a function of $\log f$), and the corresponding Bode plots showing impedance modulus ($\log|Z|$) and phase angle as a function of $\log$ frequency. The comparison illustrates the marked decrease in charge-transfer resistance, increase in interfacial admittance, enhancement in double-layer capacitance, and increased deviation from ideal capacitive behavior induced by vitamin B6 adsorption and electrochemical activity; Z_r [kohm·cm²]; $-Z_i$ [kohm·cm²]; Phase [degree].

Table 2. Comparative electrochemical impedance parameters of platinum electrodes in Na₂SO₄-based electrolytes containing vitamin B6 and silver nanoparticles.

Symbol	Na ₂ SO ₄	Na ₂ SO ₄ + B6	Na ₂ SO ₄ + B6 + nAg	Electrochemical Interpretation
OCP	0.261	0.314	0.332	Progressive positive shift indicating increasing interfacial interaction and surface modification
R_s (Ω·cm ²)	1.94	3.92	4.0	Minor changes associated with electrolyte composition and nanoparticle dispersion
R_{ct} (Ω·cm ²)	3144	234	58	Strong kinetic activation induced by vitamin B6 adsorption and silver nanoparticles
$R_p \approx R_{ct}$ (Ω·cm ²)	3144	234	58	Progressive transition from blocking to highly electroactive interface

$f_{\max}$ (Hz)	1.25	5.6	18.2	Increasing frequency response associated with faster interfacial processes
τ (s)	0.127	0.028	0.0087	Accelerated charge relaxation and electron-transfer dynamics
C_{dl} (F·cm ⁻²)	4.0×10^{-5}	1.21×10^{-4}	2.9×10^{-4}	Progressive expansion and polarization of the electrical double layer
$C_{dl}/C_{dl,Na_2SO_4}$	1.0	3.0	7.2	Increasing contribution of adsorption and pseudocapacitive processes
n (CPE exp)	0.95	0.88	0.82	Progressive deviation from ideal capacitive behavior due to adsorption-induced heterogeneity and nanoparticle-mediated surface roughness
$\varphi_{\max}$ (°)	≈ -80	≈ -60	≈ -48	Departure from ideal capacitive behavior toward mixed capacitive-faradaic response
φ_{LF} (°)	≈ -80	≈ -35	-25 to -35	Increasing contribution of pseudocapacitive and irreversible processes
YLF/YLF, Na ₂ SO ₄	1.0	≈ 2.0	≈ 4.5	Progressive enhancement in interfacial conductivity
Interfacial heterogeneity	Low	Moderate	Very high	Increasing adsorption-induced and nanoparticle-induced surface complexity
Circuit model	$R_s - (R_{ct} \parallel CPE)$	$R_s - (R_{ct} \parallel CPE)$	$R_s - (R_{ct} \parallel CPE)$	Modified Randles circuit describing heterogeneous electrochemical interfaces
Relative R_{ct} decrease	1.0	13.4	54.2	Overall enhancement in interfacial electron-transfer kinetics
Relative capacitance increase	1.0	3.0	7.2	Overall enhancement in charge-storage capability

OCP = open-circuit potential (V vs. Ag/AgCl); R_s = uncompensated solution resistance ($\Omega \cdot \text{cm}^2$); R_{ct} = charge-transfer resistance ($\Omega \cdot \text{cm}^2$); $R_p \approx R_{ct}$ = polarization resistance ($\Omega \cdot \text{cm}^2$); $f_{\max}$ = characteristic frequency at maximum phase angle (Hz); τ = interfacial relaxation time (s, $\tau = 1/\omega_{\max}$); C_{dl} = double-layer capacitance (F·cm⁻²); $C_{dl}/C_{dl,Na_2SO_4}$ = dimensionless ratio; $\varphi_{\max}$ = maximum phase angle (°); φ_{LF} = low-frequency phase angle (°); YLF = low-frequency admittance (S·cm⁻²); YLF/YLF, Na₂SO₄ = dimensionless ratio; interfacial heterogeneity = qualitative descriptor (dimensionless); circuit model = $R_s - (R_{ct} \parallel CPE)$, no physical unit. All parameters were obtained by fitting the experimental electrochemical impedance spectra using the modified Randles equivalent circuit $R_s - (R_{ct} \parallel CPE)$.

The corresponding Bode plots further support this interpretation. The impedance modulus decreases monotonically with increasing frequency and approaches the solution resistance at high frequencies. The phase angle remains close to -80° over a broad frequency range, characteristic of a nearly ideal capacitive interface governed primarily by electric double-layer charging. The calculated double-layer capacitance is approximately 4.0×10^{-5} F·cm⁻², consistent with literature values reported for clean platinum surfaces in neutral sulfate electrolytes.

Upon addition of vitamin B6, the impedance response changes dramatically (Figure 2). The Nyquist semicircle collapses substantially and the apparent charge-transfer resistance decreases by more than one order of magnitude to approximately 234 $\Omega \cdot \text{cm}^2$. Simultaneously, the solution resistance increases slightly ($R_s \approx 3.9 \Omega \cdot \text{cm}^2$), likely reflecting modest changes in electrolyte conductivity caused by interactions between sulfate ions and dissolved organic molecules.

The pronounced decrease in R_{ct} demonstrates that vitamin B6 introduces significantly more efficient interfacial charge-transfer pathways [6,7,14]. This behavior is consistent with the electroactive nature of pyridoxine and its strong adsorption on platinum surfaces. Vitamin B6 contains hydroxyl, amine, and pyridine functionalities capable of interacting with plati-

num through hydrogen bonding, electrostatic interactions, and possible π -metal interactions. These interactions modify the interfacial structure and facilitate electron-transfer processes.

The Nyquist admittance representations reveal a substantial increase in both the real and imaginary components of admittance compared with the blank electrolyte. This enhancement is particularly evident in the intermediate-frequency domain and reflects increased interfacial conductivity together with enhanced charge-storage capability. Such behavior is characteristic of pseudocapacitive systems involving surface-confined redox processes and adsorption-mediated charge transfer.

The Bode plots confirm the transition from a predominantly capacitive interface toward a mixed capacitive-faradaic regime. The phase angle decreases from approximately -80° to values near -60° , while the phase dispersion becomes considerably broader. The frequency corresponding to the maximum phase shift shifts toward higher values, indicating accelerated interfacial dynamics and reduced charge-relaxation times. The apparent double-layer capacitance increases to approximately $1.2 \times 10^{-4} \text{ F}\cdot\text{cm}^{-2}$, representing nearly a threefold enhancement relative to the Na_2SO_4 electrolyte.

This increase in capacitance reflects substantial restructuring of the electrical double layer. Adsorbed vitamin B6 molecules alter the local dielectric environment and may modify the effective thickness of the Helmholtz region, producing a more polarizable interface [38,39]. Consequently, the interfacial capacitance becomes spatially distributed and departs from ideal capacitor behavior, explaining the necessity of introducing a CPE into the equivalent circuit model.

The presence of vitamin B6 therefore transforms the platinum electrode from a predominantly blocking and capacitive interface into an electroactive and pseudocapacitive system. The concomitant decrease in apparent charge-transfer resistance, increase in capacitance, and acceleration of interfacial dynamics reveal a strong coupling between molecular adsorption and electron-transfer kinetics. These observations are fully consistent with the cyclic voltammetry results and confirm the important role of vitamin B6 in modifying the Pt/electrolyte interface.

A further and more pronounced transformation occurs after the incorporation of silver nanoparticles into the Na_2SO_4 -vitamin B6 electrolyte. The impedance spectra recorded in the presence of nAg reveal a highly conductive and electroactive interface characterized by strongly enhanced charge-transfer kinetics and pseudocapacitive behavior (Figure 3).

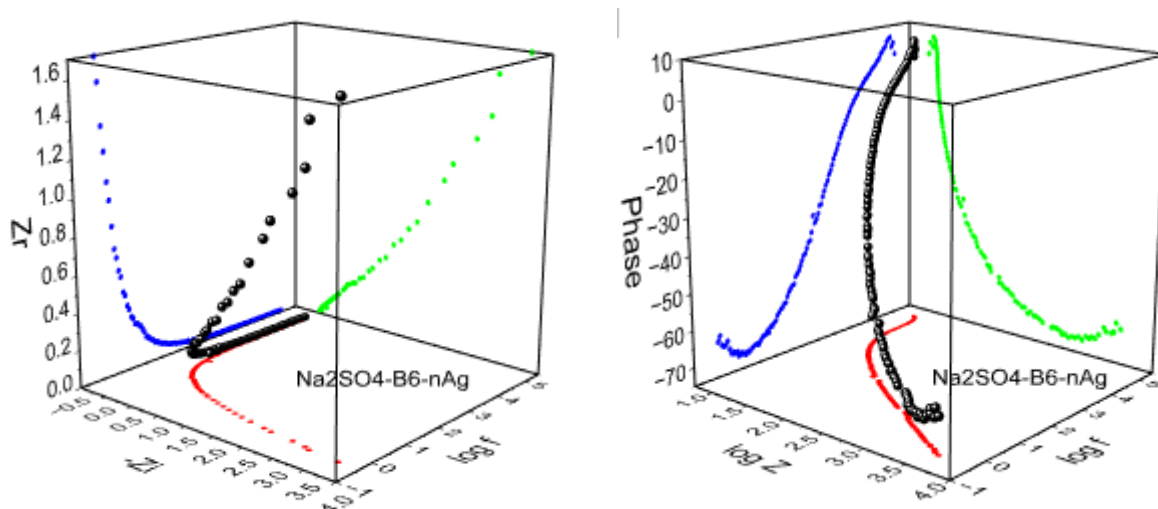


Figure 3. Three-dimensional electrochemical impedance spectroscopy (EIS) representations of a platinum working electrode (geometric area = 1 cm^2) immersed in $0.1 \text{ M Na}_2\text{SO}_4$ containing vitamin B6 ($0.05 \text{ g}\cdot\text{L}^{-1}$) and silver nanoparticles (nAg, $70 \text{ mg}\cdot\text{L}^{-1}$). Panels include Nyquist-type representa-

tions (Z_r versus $-Z_i$ as a function of $\log f$), and the corresponding Bode plots showing impedance modulus ($\log|Z|$) and phase angle as a function of $\log$ frequency. The spectra demonstrate the substantial reduction in apparent charge-transfer resistance, enhanced admittance, increased double-layer capacitance, and emergence of pronounced pseudocapacitive behavior resulting from the synergistic interaction between vitamin B6 and silver nanoparticles at the platinum/electrolyte interface.

The Nyquist plot is characterized by a strongly depressed semicircle of very small diameter, corresponding to an apparent charge-transfer resistance of approximately $58 \Omega \cdot \text{cm}^2$. This value is nearly four times lower than that measured in the vitamin B6-containing electrolyte and more than fifty times lower than that obtained in the supporting electrolyte alone. The absence of a low-frequency Warburg tail indicates that diffusion limitations remain negligible and that the electrochemical response is dominated by interfacial processes.

The Nyquist admittance representation exhibits markedly increased admittance over the entire frequency range, particularly at low and intermediate frequencies. This behavior reflects the coexistence of rapid electron-transfer processes and efficient charge storage mechanisms. The enhanced admittance confirms the formation of a highly conductive interfacial layer in which faradaic and pseudocapacitive processes occur simultaneously [22–24].

The Bode impedance plot shows a substantial reduction in impedance across the entire frequency spectrum, confirming globally accelerated interfacial kinetics. Meanwhile, the phase-angle response deviates further from ideal capacitive behavior, with a maximum phase angle near -48° and a broad phase dispersion extending across a wide frequency domain. Such behavior is characteristic of a mixed capacitive-faradaic system dominated by adsorption-mediated electron transfer and pseudocapacitive charge storage [11].

The observed behavior originates from the synergistic interaction between vitamin B6 and silver nanoparticles. Vitamin B6 molecules adsorb not only on platinum but also on nanoparticle surfaces, generating a hybrid interfacial architecture composed of Pt-B6, Ag-B6, and Pt-Ag electronic junctions. Silver nanoparticles introduce highly conductive nano-domains, increase the effective electroactive surface area, and facilitate electron transport between adsorbed species and the metallic substrate [22–24,27–29].

As a consequence, the apparent double-layer capacitance increases further to approximately $2.9 \times 10^{-4} \text{ F} \cdot \text{cm}^{-2}$, corresponding to more than seven times the capacitance measured for the blank electrolyte. This capacitance enhancement reflects expansion and polarization of the interfacial layer, increased local dielectric response, pseudocapacitive contributions from surface-confined redox-active species, and electronic coupling between platinum and silver nanoparticles.

The remarkably low charge-transfer resistance demonstrates that silver nanoparticles do not merely increase current through surface-area effects but fundamentally alter the charge-transfer mechanism operating at the interface. Several synergistic contributions may account for this behavior: (i) electronic mediation by nAg, which lowers the activation barrier for electron transfer; (ii) stabilization of intermediate oxidation states of vitamin B6; (iii) formation of conductive Pt-Ag-B6 interfacial networks; and (iv) increased pseudocapacitive charge storage associated with rapid reversible surface redox processes.

The low CPE exponent ($n < 1$), together with the broad phase-angle distribution, confirms the highly heterogeneous and adsorption-dominated nature of the interface. Multiple independent fitting procedures yielded low residuals and converged toward identical parameter values, confirming the robustness of the selected equivalent circuit model. Attempts to include a Warburg diffusion element did not improve the fitting

quality, confirming that diffusion-limited processes were negligible under the experimental conditions and that the simpler $R_s - (R_{ct} \parallel CPE)$ model adequately described the experimental spectra.

Overall, the EIS results reveal a progressive evolution of the platinum/electrolyte interface from a predominantly capacitive and blocking system in Na_2SO_4 , to an adsorption-modified electroactive interface in the presence of vitamin B6, and finally to a highly conductive, pseudocapacitive, and kinetically activated Pt-B6-nAg architecture. The systematic decrease in charge-transfer resistance, increase in capacitance, and acceleration of interfacial relaxation dynamics demonstrate the critical role of both molecular adsorption and nanoparticle-mediated electronic coupling in controlling charge-transfer processes at noble-metal electrodes.

3.3. Correlation Between Cyclic Voltammetry and Electrochemical Impedance Spectroscopy: Unified Evidence of Interfacial Activation by Vitamin B6 and Silver Nanoparticles

A combined interpretation of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) provides a comprehensive mechanistic description of the interfacial processes occurring at platinum electrodes in Na_2SO_4 -based electrolytes containing vitamin B6 and silver nanoparticles. Whereas CV probes the potential-dependent manifestation of faradaic and non-faradaic processes, EIS characterizes the same interface in the frequency domain through its charge-transfer kinetics, double-layer properties, and relaxation behavior [2,6,11]. The excellent agreement between both techniques demonstrates that the electrochemical evolution of the Pt interface follows a progressive sequence from a predominantly capacitive blocking surface in the supporting electrolyte to an adsorption-controlled electroactive interface in the presence of vitamin B6 and, finally, to a highly conductive hybrid metal–organic system after incorporation of silver nanoparticles.

Although the present study does not provide direct spectroscopic or gravimetric evidence of adsorption (e.g., EQCM, SERS or in situ infrared spectroscopy), several independent electrochemical observations consistently support an adsorption-mediated interfacial mechanism. These include (i) the pronounced decrease in apparent charge-transfer resistance, (ii) the simultaneous increase in apparent double-layer capacitance, (iii) the emergence of irreversible anodic currents, (iv) the deviation from ideal capacitive behavior reflected by the CPE exponent, and (v) the excellent correlation between cyclic voltammetry and impedance spectroscopy. While these observations do not constitute direct proof of adsorption, they are collectively most consistent with specific interfacial interaction of vitamin B6 with the platinum surface rather than with a purely homogeneous redox process occurring exclusively in the bulk electrolyte.

In 0.1 M Na_2SO_4 , platinum exhibits the characteristic behavior of a clean noble-metal electrode. The cyclic voltammograms display nearly symmetric anodic and cathodic charges ($+Q \approx 0.028$ C; $-Q \approx 0.031$ C), yielding a Q_a/Q_c ratio close to unity, indicative of reversible double-layer charging and platinum surface oxidation/reduction with negligible contribution from irreversible faradaic reactions. These observations are fully supported by the EIS results, which reveal a large Nyquist semicircle corresponding to an apparent charge-transfer resistance of approximately $3.14 \text{ k}\Omega\cdot\text{cm}^2$ and a relatively small double-layer capacitance ($C_{dl} \approx 4.0 \times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$). The absence of a Warburg diffusion tail, together with a phase angle approaching -80° over a broad frequency range, confirms that the interface behaves predominantly as a capacitive blocking electrode. Under these conditions, sulfate ions act essentially as inert supporting electrolyte species, preserving a classical Gouy–Chapman–Stern electrical double layer with minimal perturbation of the platinum surface.

The addition of vitamin B6 fundamentally changes this electrochemical behavior. Cyclic voltammetry reveals a marked increase in anodic charge ($+Q \approx 0.088$ C), whereas the cathodic charge increases only moderately ($-Q \approx 0.041$ C), resulting in a Q_a/Q_c ratio of approximately 2.1. This pronounced charge imbalance demonstrates the activation of irreversible or quasi-reversible oxidation processes associated with adsorbed vitamin B6 species. The voltammetric response is directly corroborated by the impedance measurements, which show that the apparent charge-transfer resistance decreases by more than one order of magnitude, from approximately 3144 to 234 $\Omega\cdot\text{cm}^2$, while the apparent double-layer capacitance increases nearly threefold to approximately 1.2×10^{-4} $\text{F}\cdot\text{cm}^{-2}$.

The excellent correspondence between these parameters demonstrates that the increased anodic currents observed in CV originate from kinetically accelerated faradaic oxidation rather than from purely capacitive charging. Simultaneously, the increase in C_{dl} mirrors the enhanced non-faradaic currents, confirming that vitamin B6 adsorption restructures the electrical double layer while promoting electron-transfer reactions through a common adsorption-driven mechanism. The reduced maximum phase angle ($\approx -60^\circ$), broad phase dispersion, higher characteristic frequency, and shorter interfacial relaxation time ($\tau \approx 0.028$ s) further demonstrate the transition from a nearly ideal capacitive interface toward a mixed capacitive-faradaic regime. The requirement to model the interface using a constant phase element (CPE) additionally confirms the development of adsorption-induced interfacial heterogeneity.

These complementary observations demonstrate that vitamin B6 is not merely an electroactive solute but an effective interfacial modifier. Through adsorption involving its hydroxyl, amine, and pyridine functional groups, vitamin B6 displaces interfacial water molecules, alters the local dielectric environment, modifies the effective thickness of the Helmholtz layer, and introduces new electronic states capable of participating in charge transfer. Consequently, adsorption simultaneously lowers the apparent charge-transfer resistance, increases the apparent double-layer capacitance, and activates surface-confined redox reactions. The excellent correlation between the decrease in R_{ct} and the increase in anodic charge provides compelling evidence that adsorption-mediated electron transfer is the dominant mechanism governing the Pt|Na₂SO₄|vitamin B6 interface.

An even more pronounced interfacial activation occurs following the incorporation of silver nanoparticles. Cyclic voltammetry shows a substantial increase in both anodic and cathodic currents, accompanied by improved charge symmetry and enhanced charge recovery compared with the vitamin B6-only electrolyte. These observations indicate that the interface evolves from an adsorption-dominated, partially irreversible system toward a mixed faradaic-pseudocapacitive regime characterized by faster and more reversible charge exchange.

Electrochemical impedance spectroscopy quantitatively confirms this transformation. The apparent charge-transfer resistance decreases further to approximately 58 $\Omega\cdot\text{cm}^2$, while the apparent double-layer capacitance increases to approximately 2.9×10^{-4} $\text{F}\cdot\text{cm}^{-2}$, more than seven times larger than that of the supporting electrolyte. The corresponding interfacial relaxation time decreases to only 8.7 ms, demonstrating exceptionally rapid charge-transfer dynamics. Simultaneously, the Nyquist spectra exhibit a highly compressed semicircle, the impedance modulus decreases over the entire frequency range, and the admittance markedly increases, indicating the formation of a highly conductive interface. The broad phase-angle distribution, depressed Nyquist semicircle, and continued requirement for a constant phase element demonstrate that this highly active interface remains strongly heterogeneous due to molecular adsorption and nanoparticle-induced surface roughness [22–24].

The direct correspondence between CV and EIS becomes particularly evident after addition of silver nanoparticles. The enhanced anodic and cathodic currents observed in cyclic voltammetry correlate closely with the ultralow charge-transfer resistance extracted from impedance measurements, demonstrating that the current amplification originates from accelerated electron-transfer kinetics rather than from increased capacitive charging alone. Likewise, the larger capacitive currents observed in the non-faradaic potential region correspond directly to the substantially increased apparent double-layer capacitance determined by EIS, confirming the emergence of a hybrid charge-storage mechanism in which classical electrical double-layer charging coexists with pronounced pseudocapacitive contributions.

These observations demonstrate that silver nanoparticles play a dual role within the interfacial layer. Besides increasing the effective electroactive surface area, they introduce conductive nano-domains and additional electronic pathways that facilitate charge transport between adsorbed vitamin B6 molecules and the platinum substrate. Such electronic coupling lowers the activation barrier for electron transfer, stabilizes intermediate oxidation states, promotes rapid electron delocalization, and partially suppresses irreversible charge-consumption pathways. Consequently, the interface exhibits simultaneously enhanced faradaic activity, increased charge-storage capability, and improved electrochemical reversibility.

The electrochemical results are further supported by the optical characterization. The pronounced red-shift in both the low-energy and high-energy optical transitions observed in the UV-Vis/Tauc analysis after addition of silver nanoparticles is fully consistent with the ultralow charge-transfer resistance and enhanced admittance measured by EIS. These parallel trends indicate that the emergence of low-energy optical transitions and the acceleration of interfacial electron transfer originate from the same fundamental mechanism, namely the formation of metal–organic charge-transfer states resulting from electronic coupling between vitamin B6 and silver nanoparticles.

Overall, the combined CV, EIS, and UV-Vis/Tauc results provide a coherent and internally consistent mechanistic picture of the Pt|Na₂SO₄ interface. In the supporting electrolyte, platinum behaves as a classical blocking electrode governed primarily by electrostatic double-layer charging and reversible surface oxidation. Adsorption of vitamin B6 restructures the electrical double layer, increases interfacial capacitance, lowers the apparent charge-transfer resistance, and activates adsorption-mediated faradaic reactions. The subsequent incorporation of silver nanoparticles transforms this adsorption-controlled interface into a highly conductive hybrid metal–organic architecture in which electronic coupling between platinum, vitamin B6, and silver nanoparticles simultaneously enhances charge storage, accelerates electron-transfer kinetics, and lowers the energy required for optical excitation. The remarkable agreement between time-domain (CV), frequency-domain (EIS), and spectroscopic (UV-Vis/Tauc) observations demonstrates that adsorption-driven interfacial reorganization and metal–organic electronic coupling constitute the fundamental mechanisms governing both the electrochemical and optical behavior of the investigated systems.

3.4. Optical Properties and Tauc Analysis of Na₂SO₄-Vitamin B6-*n*Ag Systems

The application of the Tauc formalism in the present study is intended as a phenomenological approach for estimating characteristic optical transition energies rather than true electronic band gaps in the solid-state sense. While the Tauc model was originally developed for amorphous and crystalline semiconductors, it has been widely employed in the literature to analyze the optical absorption behavior of molecular systems, coordination complexes, colloids, and hybrid metal–organic systems in solution, where electronic transitions give rise to quasi-linear absorption onsets.

In such systems, the extracted Tauc energies do not represent fundamental band gaps but instead reflect effective optical transition thresholds, associated with molecular electronic transitions, charge-transfer states, defect-like states, or hybridized electronic levels [28,29]. The assumption of direct allowed transitions ($n = 2$) is justified by the dominance of dipole-allowed electronic transitions ($\pi-\pi^*$, $n-\pi^*$, and metal–ligand or metal–molecule charge-transfer transitions) in organic and hybrid systems [30–34].

Importantly, the Tauc-derived quantities reported throughout this work are not interpreted as semiconductor band gaps or fundamental electronic structure parameters. Instead, they are treated as empirical descriptors of the optical absorption edge, allowing for a consistent comparison of the progressive evolution of the optical response upon addition of vitamin B6 and silver nanoparticles. Their physical significance therefore lies in tracking relative shifts in the apparent absorption onset associated with changes in molecular electronic transitions, charge-transfer interactions, and hybrid metal–organic electronic states, rather than in determining absolute band-gap energies.

The optical properties of the investigated electrolytes were examined using UV-Vis absorption spectroscopy, and the characteristic optical transition energies were empirically estimated using the Tauc formalism as apparent optical transition energies.: $(\alpha h\nu)^2 = A(h\nu - E_{\text{optic}})$, where α is the absorption coefficient, $h\nu$ is the photon energy, A is a proportionality constant, and E_{optic} represents the apparent optical transition energy.

Two distinct optical transition energies were extracted for each system:

- E_{low} , obtained from the low-energy linear region near the absorption onset, associated with low-energy electronic transitions, charge-transfer states, or intermolecular interactions;
- E_{high} , obtained from the higher-energy linear region, corresponding to intrinsic electronic transitions of the molecular or hybrid system.

The optical properties of the Na_2SO_4 -based electrolytes were thus analyzed using Tauc plots derived from UV-Vis absorption spectra, allowing for the determination of these two characteristic optical transition energies. Together, E_{low} and E_{high} provide complementary insight into the emergence of low-energy electronic states and the modification in intrinsic molecular transitions upon the addition of vitamin B6 and silver nanoparticles.

The reference electrolyte, 0.1 M Na_2SO_4 , exhibits optically inert behavior, as evidenced by weak absorption confined to the deep ultraviolet region. The corresponding Tauc plot (Table 3) does not show a well-defined low-energy linear region, resulting in a large and poorly resolved E_{low} (≥ 3.8 eV). The high-energy optical transition energy, E_{high} , is approximately 4.6 eV and can be attributed primarily to solvent–electrolyte background transitions. These values confirm that sulfate ions do not introduce accessible electronic states in the near-UV or visible range and therefore constitute an electronically passive medium.

The introduction of vitamin B6 into the sulfate electrolyte leads to a pronounced modification in the optical response [30–34]. The Tauc analysis reveals the appearance of two distinct linear regions (Table 3), enabling the extraction of both E_{low} and E_{high} . In this system, E_{low} decreases significantly to approximately 2.9 eV, while E_{high} is reduced to about 4.1 eV. The emergence of a lower-energy optical transition reflects the introduction of localized electronic states associated with molecular $n-\pi^*$ and $\pi-\pi^*$ transitions of vitamin B6, as well as weak intermolecular interactions with the aqueous environment. The relatively large separation between E_{low} and E_{high} indicates that these electronic states remain largely molecular in character, with limited electronic delocalization in the sulfate medium.

A markedly different optical response is observed upon the addition of silver nanoparticles to the Na₂SO₄-vitamin B6 system. The presence of nAg induces a further and substantial reduction in both optical transition energies, with E_{low} decreasing to approximately 2.2 eV and E_{high} to about 3.7 eV. Relative to the vitamin B6-only system, E_{low} is lowered by nearly 0.7 eV, while E_{high} decreases by approximately 0.4 eV. This simultaneous shift in both transition energies is consistent with the emergence of additional electronic states associated with metal–organic interactions [30–35].

Table 3. Apparent optical transition energies (E_{low} and E_{high}) estimated from Tauc analysis.

Electrolyte System	E_{low} (eV)	E_{high} (eV)	Electronic/Optical Assignment
Na ₂ SO ₄	≥ 3.8	4.6 ± 0.1	Optically inert electrolyte; deep-UV transitions
Na ₂ SO ₄ + vitamin B6	2.9 ± 0.1	4.1 ± 0.1	Molecular electronic states of vitamin B6
Na ₂ SO ₄ + vitamin B6 + nAg	2.2 ± 0.1	3.7 ± 0.1	Hybrid metal–organic charge-transfer states

The pronounced decrease in E_{low} in the presence of silver nanoparticles reflects the introduction of low-energy charge-transfer transitions, likely originating from electronic coupling between the molecular orbitals of vitamin B6 and the surface electronic states of nAg. Such coupling enables electronic transitions at lower photon energies, extending absorption toward the visible region. Concurrently, the reduction in E_{high} indicates that the intrinsic electronic structure of vitamin B6 is perturbed by interaction with the metallic surface, consistent with increased electronic interaction and partial electronic delocalization at the metal–organic interface.

The systematic evolution of E_{low} and E_{high} across the three systems—Na₂SO₄, Na₂SO₄ + vitamin B6, and Na₂SO₄ + vitamin B6 + nAg—demonstrates a clear progression from an optically inert electrolyte to a molecularly active system and, finally, to a hybrid metalorganic electronic structure [30–35]. The role of silver nanoparticles is therefore not merely additive but transformative, as they fundamentally alter the electronic landscape by enabling low-energy electronic transitions that are inaccessible in the absence of the metal component.

These optical results strongly complement the electrochemical findings discussed in the CV and EIS sections, where the presence of vitamin B6 and nAg leads to enhanced charge-transfer kinetics and increased interfacial activity. Taken together, the combined spectroscopic and electrochemical evidence indicates that silver nanoparticles act as effective electronic mediators, promoting charge-transfer interactions and lowering the energetic threshold for electronic excitation in vitamin B6-modified electrolytes.

In conclusion, the Tauc analysis reveals a systematic decrease in the apparent optical transition energies upon incorporation of vitamin B6 and silver nanoparticles, with E_{low} decreasing from ≥ 3.8 eV in the blank electrolyte to approximately 2.2 eV in the hybrid system (Table 3). This evolution provides spectroscopic support for progressive metal–organic electronic interactions and is consistent with the formation of hybrid electronic states involving vitamin B6 and silver nanoparticles.

The systematic decrease in both E_{low} and E_{high} across the three systems—Na₂SO₄, Na₂SO₄ + vitamin B6, and Na₂SO₄ + vitamin B6 + nAg—reveals a progressive electronic activation of the electrolyte environment. In the blank sulfate solution, the absence of accessible low-energy transitions confirms its electronically inert character. The introduction of vitamin B6 generates localized molecular electronic states, lowering E_{low} and enabling weak intermolecular charge-transfer excitations.

The further and substantial red-shift induced by silver nanoparticles provides strong spectroscopic indication for the formation of hybrid metal–organic electronic states. The results suggest electronic interactions between the silver nanoparticles and the adsorbed vitamin B6 molecules at the electrode interface. These interactions may arise from several mechanisms, including nanoparticle-induced conductivity enhancement, plasmonic effects, or interfacial electronic coupling. A definitive demonstration of orbital hybridization would require complementary spectroscopic or theoretical investigations.

Importantly, these optical changes are not merely spectroscopic curiosities but are directly linked to the enhanced electrochemical functionality of the interface. The same metal–organic coupling mechanism that lowers E_{low} and E_{high} also gives rise to ultrafast interfacial kinetics, ultralow R_{ct} , and strong pseudocapacitive behavior, thereby establishing a direct causal connection between optical excitation pathways and electrochemical charge-transfer dynamics.

4. Conclusions

This work provides a unified electrochemical–optical framework for understanding the influence of vitamin B6 adsorption and silver nanoparticles on the interfacial behavior of platinum electrodes in sulfate electrolytes. By combining cyclic voltammetry, electrochemical impedance spectroscopy, and UV-Vis/Tauc analysis, this study demonstrates that the electrochemical and optical responses evolve consistently with progressive modification in the Pt/electrolyte interface.

In the supporting electrolyte, platinum behaves predominantly as a blocking electrode governed by double-layer charging and reversible surface processes. The addition of vitamin B6 modifies the electrical double layer through adsorption-induced interfacial reorganization, resulting in lower apparent charge-transfer resistance, increased interfacial capacitance, and activation of surface-confined electrochemical reactions. Incorporation of silver nanoparticles further enhances these effects, producing a highly conductive hybrid interface characterized by faster charge-transfer kinetics, enhanced pseudocapacitive behavior, and lower apparent optical transition energies. The strong agreement between CV, EIS, and UV-Vis/Tauc results supports the proposed adsorption-mediated interfacial activation and electronic interaction between vitamin B6 and silver nanoparticles.

The present findings demonstrate that coupling biomolecular adsorption with metallic nanoparticles represents an effective strategy for tuning charge storage, charge transfer, and optical response at electrified interfaces. These insights are relevant for the rational design of advanced electrochemical sensors, hybrid bioelectronic interfaces, and functional electrocatalytic materials.

The present study has some limitations. The adsorption mechanism was inferred from the combined electrochemical and spectroscopic observations rather than directly demonstrated using surface-sensitive techniques, and the long-term stability of the Pt–vitamin B6–Ag nanoparticle interface under extended electrochemical cycling was not systematically investigated, although the electrochemical response remained reproducible throughout the experimental measurements.

Future work should therefore combine the present electrochemical methodology with complementary surface-sensitive techniques, such as electrochemical quartz crystal microbalance (EQCM), surface-enhanced Raman spectroscopy (SERS), in situ infrared spectroscopy, or X-ray photoelectron spectroscopy (XPS), together with long-term stability studies, to directly verify the proposed adsorption mechanism and further elucidate the molecular origin of the observed interfacial electronic coupling.

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