

## Surface pKa determination of benzoic acid modified gold electrode by electrochemical and contact angle measurement methods

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**Abstract** pKa values of the organic surfaces were determined with ionizable carboxylic acid groups, obtained by the modification of gold electrode by reduction of p-benzoic acid diazonium tetrafluoroborate and oxidation of p-aminobenzoic acid. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques were used in the surface pKa determination, by exploiting the barrier effect arising from the charged nature of the surface against the electrochemistry of Fe(CN)<sub>6</sub><sup>4-/3-</sup> redox probe. Contact angle measurement (CAM) technique was also used to compare the accuracy of the surface pKa values acquired by electrochemical methods. pKa values for Au-BA were found as 2.938±0.283, 4.128 ± 0.342 and 4.251±0.089 by CV, EIS, and CAM, respectively; while the values are 4.084±0.101 5.326±0.323 and 5.102±0.147 for Au-NHBA.

**Keywords** Surface pKa of benzoic acid; modified gold electrode; cyclic voltammetry; electrochemical impedance spectroscopy; contact angle measurement

### Benzoik Asitle Modifiye Edilmiş Altın Elektrotun Yüzey pKa'sının Elektrokimyasal ve Temas Açısı Ölçüm Metotları ile Tayini

**Özet** p-Benzoik asit diazonyum tuzunun altın elektrot yüzeyinde indirgenmesi ile p-amino benzoik asit tuzunun yükseltgenmesi sonucu elde edilen modifiye altın elektrot yüzeylerinin pKa değerleri iyonize olabilen karboksilik asit grupları ile tayin edilmiştir. pKa tayini için dönüşümlü voltametri (CV) ve elektrokimyasal empedans spektroskopisi (EIS) teknikleri kullanılmıştır. Redoks probu olarak Fe(CN)<sub>6</sub><sup>4-/3-</sup> kullanılmıştır. Elektrokimyasal tekniklerle belirlenen pKa değerlerini karşılaştırmak amacıyla temas açısı ölçümleri (CAM) yapılmıştır. Au-BA için pKa değerleri CV, EIS ve CAM teknikleri ile sırasıyla 2.938±0.283, 4.128 ± 0.342 ve 4.251±0.089 ve Au-NHBA için ise yine sırasıyla 4.084±0.101 5.326±0.323 ve 5.102±0.147 olarak bulunmuştur.

**Anahtar sözcükler:** Benzoik asitin yüzey pKa, modifiye altın elektrot, dönüşümlü voltametri, elektrokimyasal empedans spektroskopisi, temas açısı ölçümü

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## 1. INTRODUCTION

Electrografting of organic molecules is generally carried out on metal, carbon or semiconductor surfaces[1,2] by oxidation of amines[3,4], polymerization[5,6] and diazonium salt reduction[7-9] to form covalent carbon-carbon, nitrogen-carbon or metal-carbon bonds at the surfaces. In all of these grafting processes, principally radicals are formed by the way of electrochemical oxidation or reduction, and these radicals interact immediately with the active sites of the electrode surfaces[10].

In general, modification can be carried out by changing the chemical and physical properties of the electrode using electrochemical or chemical techniques. In most cases, nano scale films are formed at the electrode surfaces and these surfaces are used to protect the materials from corrosion, understand the electrochemical electron transfer rates, manufacture sensing electrodes and form molecular junctions [11,12]. For example, McCreery's group reported that modifying Cu and Al alloy 2024 T3 surfaces with aryl diazonium salts protect the surfaces from corrosion by inhibiting oxygen reduction [13]. Molecular junctions formed from the modified surfaces with specific properties are also used to manufacture molecular electronic devices [14,15]. Another utilization of the modified surfaces is the area of biosensors in which biomolecules are used as modifying compounds [16].

Among various modification methods, the most economic and the easiest one is the diazonium salt (DAS) reduction[2,8,17-20] and oxidation of amines to form covalent bonds at the carbon or metal surfaces [3,4]. Surface modification of glassy carbon [2,19,21,22], platinum [7,23], gold [20,24], copper [13], iron [25,26], silicon [7], GaAs and palladium [27] by diazonium salt reduction have been reported in the literature. This kind of modified surfaces can be characterized by redox probe electrochemistry[28], X-ray photoelectron spectroscopy[18,29], Raman spectroscopy[30], reflectance infrared spectroscopy[31], ellipsometry[7], contact angle measurement [32] and microscopic techniques [33].

The knowledge of the acid/base properties and proton transfer abilities of surfaces is essential for various investigations at the modified surfaces especially in analytical studies [34-36] and molecular junctions [37]. Various methods have been developed to measure the pKa values of modified surfaces which are essential to diverse applications such as wetting, biological interactions and sensing [37]. These methods include differential interfacial capacitance, contact angle, mass change, force titration, surface enhanced Raman scattering, a laser-induced temperature jump, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) [37]. Among them electrochemical methods, EIS and CV, are more simple and are based on the charge transfer resistance and the current responses of an electroactive redox probe such as Fe(CN)<sub>6</sub><sup>3-</sup>, respectively. On the other hand contact angle measurements (CAM) are based on the consideration of a thermodynamic equilibrium between the solid surface and the liquid phase.

Various studies have been reported in the literature on modified surfaces bearing acidic functionalities at either GC or metals [34-38]. These surfaces mostly with weak acidic behavior impart charge selectivity properties in basic media. Yang et al. reported that they modified GC electrode with 4-aminobenzoic acid via electrochemical amine oxidation in aqueous solution, and resulted in a quite stable film which was used as a precursor substrate for construction of copper hexacyanoferrate multilayer films [34]. Liu et al. reported that, 4-aminobenzoic acid was covalently electrografted on a GC electrode by amine cation radical formation and the effect of pH changes on the modified surface was studied for the purpose of surface pKa determination [35]. In another paper Li et al. determined the surface pKa of *r*-aminobenzene sulphonic acid modified GC surface using CV and EIS.[39] Bryant et al. reported that, they modified Au electrode with 4-mercaptopyridine (4-MP) and 4-aminothiophenyl molecules and presented a new method for in situ electrochemical measurement of surface pKa values as a function of the electrode potential [36]. Kim et al. investigated that proton transfer reaction was performed at the

interface of the Au electrode by pure 3-mercaptopropionic acid and ethanethiol mixture. pKa of the mercaptopropionic acid molecules on the gold electrode surface prepared as a self assembly monolayer (SAM) was determined as 6.0 [37]. In an earlier paper we prepared a benzoic acid nanofilm at a glassy carbon electrode and characterized the surface by reflectance FT-IR using a new statistical approach to reach optimal smoothing [40]. In another study, we prepared a benzoic acid- and p-aminobenzoic acid-modified platinum surfaces by electrochemical reduction and determined pKa values of modified platinum surfaces via electrochemical and contact angle measurements [41].

In the present paper, polycrystalline gold electrode surface was modified by reducing BADAS in non-aqueous medium and the oxidation of p-aminobenzoic acid in aqueous medium. Then, pKa values of the benzoic acid and p-aminobenzoic acid films at the Au electrodes were determined using fundamentally three different techniques, CV, EIS, and CAM. These surface pKa values obtained by these techniques were compared. To achieve these tasks, a series of buffer solutions with different pH values are used to investigate the dissociation of surface confined –COOH groups.

## **2. EXPERIMENTAL**

### **2.1. Apparatus and Chemicals**

Analytical grade p-aminobenzoic acid (Sigma), tetrafluoroboric acid and tetrabutylammonium tetrafluoroborate (Aldrich), sodium nitrite and acetonitrile (Sigma-Aldrich), potassium chloride, sodium hydroxide, isopropyl alcohol and acetic acid (Riedel), potassium ferricyanide and potassium ferrocyanide (Merck) and diethyl ether (Fluka) were purchased and used without further purification. Britton-Robinson (BR) buffer solutions were prepared by mixing boric acid, phosphoric and acetic acid in 0.1 M KCl and pH was adjusted by adding proper amount of sodium hydroxide solution. All experiments were carried out using ultra pure quality of water with a resistance of ~18.3 MΩ cm (obtained from Human Power 1+ Scholar purification system).

All electrochemical experiments were performed using Gamry Reference 600 workstation. Working electrode was a bare (BAS, MF-2014) or modified gold disc electrode. A platinum wire was used as a counter electrode. In aqueous media Ag/AgCl/KCl(sat), in non-aqueous media Ag/Ag+(0.01 M AgNO<sub>3</sub>) electrodes were used as reference. All pH measurements were performed using an ORION SA-720 pH-meter.

Contact angle measurements were performed with an automatic contact angle analyzer (DSA 100, Krüss, Germany) at room temperature. The volume of the drop was 5 μL in all measurements. The contact angles were calculated using DSA3 software of the instrument. The values of contact angle measurements were the average of at least five values.

A sinusoidal potential modulation of 10 mV amplitude was superimposed on a fixed dc. potential and amplitude and phase angle of the resulting current were recorded at frequencies ranging from 100 kHz to 0.1 Hz.

EIS measurements were performed using a Gamry Reference 600 workstation in conjunction with EIS 300 software. EIS data were recorded between 0.1 Hz and 300 kHz frequencies. EIS experiments were carried out in the presence of 2 mM Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> redox couple containing 0.1 M KCl at different pH values. The dc potential was set up at the formal potential of redox couple. The EIS data was studied using Echem Analyst software and were analyzed by non-linear least squares (NLLS) fitting to the theoretical model represented by an equivalent electrical circuit.

Surface pKa values of benzoic acid modified gold electrode were determined by CV, EIS in 2 mM Fe(CN)<sub>6</sub><sup>3-</sup> and 2 mM Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> solutions, respectively, in BR buffer solution at different pH value and in HCl when the pH is less than 2.

## 2.2. Preparation and Modification of the Gold Disc Electrodes

Benzoic acid diazonium salt was synthesized from p-aminobenzoic acid as described in the literature [15]. FTIR characterization of the benzoic acid diazonium salt was performed using Bruker Tensor 27. Prior to modification processes, gold disc electrodes were sandpapered with 4000-grained emery paper and polished with 1.0 μM, 0.3 μM and 0.05 μM alumina slurry (Baikowski Int. Corp. USA) on a microcloth pad (Buehler, Lake Bluff, IL, USA). The electrodes were sonicated in ultra pure water for 10 minutes and then placed in 1:1(v/v) isopropyl alcohol/acetonitrile (IPA/CH<sub>3</sub>CN) mixture purified over activated carbon and sonicated 10 minutes again. After being polished, benzoic acid modified gold electrode (Au-BA) was prepared with a solution of 1 mM p-benzoic acid diazonium tetrafluoroborate (BA-DAS) in CH<sub>3</sub>CN containing 0.1 M tetrabutyl-ammonium tetrafluoroborate (TBATFB). CV experiments were performed in the potential range from 0.5 V to -0.80 V vs. Ag/Ag<sup>+</sup> (0.01 M) reference electrode with a scan rate of 200 mV/s for 10 cycles. Before modification the diazonium salt solution was purged at least 10 min.

Modification of gold electrodes with p-ABA via amine oxidation was performed in 5 mM p-ABA in 0.1 M KCl solution. CV was performed from 0.7 V to 1.20 V vs. Ag/Ag<sup>+</sup>(0.01 M) reference electrode with a scan rate of 200 mV/s for 10 cycles. Following the modification, to determine the surface pKa values of modified electrodes, CV measurements was carried out in -0.4 V and +0.8 V potential range with a 100 mV/s scan rate at different pH values, containing 2 mM K<sub>3</sub>Fe(CN)<sub>6</sub> as a redox probe and 0.1 M KCl as a supporting electrolyte. The anodic/cathodic peak currents were determined from the voltammogram of the redox probe and then the pKa value of the modified electrode was calculated from the inflection point of the I<sub>p</sub>-pH curve.

## 3. RESULTS and DISCUSSION

### 3.1. Modification of Gold Electrode with Benzoic Acid

Gold surface was modified with benzoic acid nanofilm by reducing 1 mM BA-DAS in acetonitrile (0.1 M TBATFB) and oxidation of 5 mM p-ABA in 0.1 M KCl solution. Modification voltammograms are shown in Figure 1 for both modification processes. In the BA-DAS reduction voltammogram, the first scan showed a characteristic reduction peak at 250 mV vs. Ag/Ag<sup>+</sup> indicating the formation of 4-carboxyphenyl radicals which then covalently bind to the gold surface [42]. As Figure 1a shows, peak current decreases as the number of potential cycle increases and reaches to a steady-state condition after ten cycles, implying the formation of the BA blocking layer as the number of potential cycles increases. This current–potential behavior shows the characteristic features of electrochemical reduction of diazonium salts at carbon and metal electrodes in aqueous and nonaqueous media [7,9,21,43]. It is well known that various organic molecules are covalently linked directly to the carbonaceous surfaces through C-C bonds when the solutions of the aryl diazonium salts are reduced [20,44,45]. The DAS reduction method can also be applied to the metal surface modification in which formation of strong bonds, most likely covalent, between the metal and an organic molecule are observed [9,42].

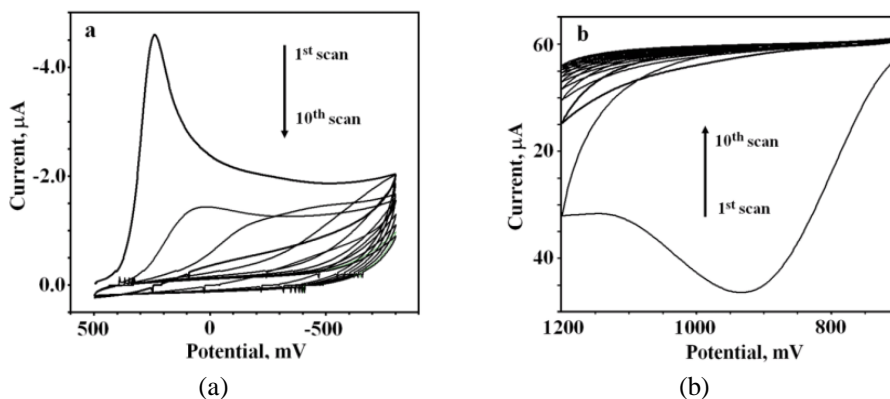
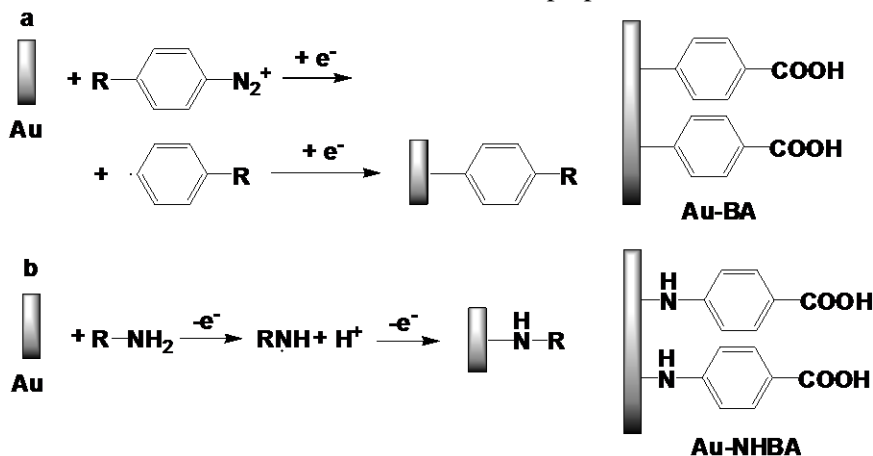


Figure 1. Modification voltammograms of the gold surface by cyclic voltammetry for (a) the reduction of 1 mM BA-DAS in acetonitrile (0.1 M TBATFB) and (b) the oxidation of 5 mM p-ABA in 0.1 M KCl solution. Scan rate was 200 mV/s for 10 CV cycles in each case.

In the p-ABA oxidation voltammogram, as Figure 1b shows, there is an irreversible oxidation peak at 925 mV assigned to p-ABA oxidation and on repeat scans the peak current decreases and is absent by the 10th cycle. The mechanism of modification of carbon and metal surfaces by the oxidation of primary amines is also well-established, in which C–N covalent bond is formed on carbon and Me–N bond on metal surfaces [9,10]. Grafting mechanism in aqueous solution depends on the formation of cation radical that deprotonates giving a C-centered radical, followed by isomerisation to an amino radical which covalently couples to the surface [28,46]. Modification mechanism and structure of Au-BA and Au-NHBA surfaces are given schematically in Scheme.

Au-BA and Au-NHBA surfaces were characterized using ferrocene and dopamine solutions (1mM each) as redox probes and the reversible cyclic voltammetric peaks of ferrocene and dopamine observed at the unmodified gold surface were almost completely suppressed at the modified surfaces. Voltammograms of these redox probes gave strong evidence that benzoic acid nanofilm was formed at the gold surface. The characterization of a benzoic acid and isophthalic acid films on the carbon surface is discussed in our earlier papers [40,47], and in a paper published by Gooding's group on gold surface [42] in detail. So no further discussion on the characterization of surfaces will be given in this paper. In reality, the following parts of this paper can also be considered as the characterization of the surfaces prepared.



Scheme - Modification mechanism and structure of Au-BA and Au-NHBA surfaces.

### 3.2. pKa determination of Au-BA and Au-NHBA surfaces by cyclic voltammetry

Acid dissociation constants for the modified gold surfaces, Au-BA and Au-NHBA, were determined by CV in a 2 mM aqueous solution of  $\text{Fe}(\text{CN})_6^{3-}$ . Voltammograms of this redox probe were acquired in BR buffer solutions of different pH values between 2 and 12. Figure 2 shows a series of cyclic voltammograms of  $\text{Fe}(\text{CN})_6^{3-}$  on Au-BA surface vs. pH of BR buffer solution (in 0.1 M KCl). Since the pKa of the  $-\text{COOH}$  groups in the bulk solution is not much affected by the ionic strength, while the pKa of the surface-confined  $-\text{COOH}$  groups is highly dependent on the ionic strength changes[37], ionic strength of the BR buffer is kept constant by preparing it in 0.1 M KCl electrolyte. Cathodic peak currents at different pH values were measured for each of four different Au-BA and Au-NHBA electrodes. pKa values of the surface films were determined by CV according to the procedure reported elsewhere.[39,48] This procedure is based on the surface charge states of the modified electrodes which determine the diffusion current for the reduction of negatively charged  $\text{Fe}(\text{CN})_6^{3-}$  ions. Therefore, the current response of the redox probe is related to the charge state of the surface which is determined by the pH of the buffer solutions. In buffer solutions with pH greater than pKa value of the surface, the  $-\text{COOH}$  groups will dissociate and impart a negative charge to the surface. On the other hand, when the pH of the buffer solution is lower than the pKa, the surface confined  $-\text{COOH}$  groups cannot dissociate and the surface of the electrode will be uncharged and fully protonated form. On the uncharged surface, ferricyanide ions can easily exchange electrons with the gold surface exhibiting well-defined CV waves. Conversely, on the negatively charged surface, the repulsive electrostatic forces between the surface and the negatively charged ions operate effectively sending away the redox probe anions.[34] Therefore, when the pH of the solution increases, diffusion current gradually decreases from a plateau and reaching again a plateau, due to the complete dissociation of the carboxylic acid groups on the surface film on which electron transfer is blocked.

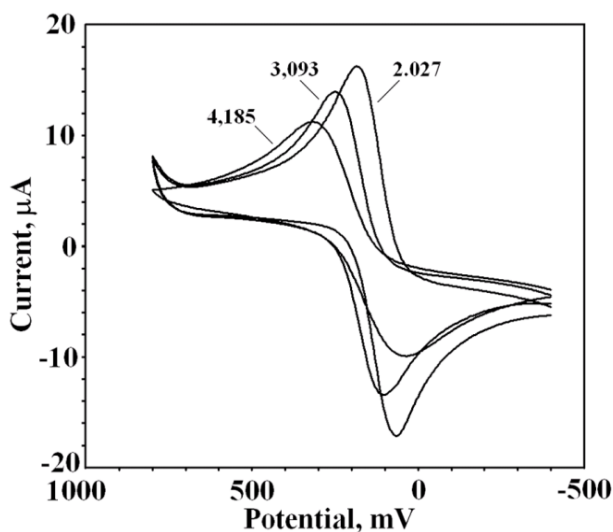


Figure 2. Cathodic peak currents of  $\text{Fe}(\text{CN})_6^{3-}$  ions on Au-BA surface vs. pH of BR buffer in 0.1 M KCl solution. Scan rate is 100 mV s<sup>-1</sup>.

Cathodic peak currents of the ferricyanide ions on these surfaces versus pH of BR buffer solution are plotted and given in Figure 3. As Figure 3 shows, surface pKa values were obtained from the inflection points of the fitted current-pH curves and also from the peaks of their derivatives. pKa of the carboxylic acid groups at the surface films are estimated to be



2.938±0.283 for Au-BA and 4.084 ± 0.101 for Au-NHBA surfaces. Here, it should be noted that the pKa values of both Au-BA and Au-NHBA surfaces measured by CV are lower than that of benzoic acid (4.20) [44,49,50] and p-aminobenzoic acid (4.60) [35,51] in bulk solution. Interestingly, pKa values shifted to lower values more than 1.3 pKa units for Au-BA and 0.5 for Au-NHBA reference to the pKa values of the same species in bulk solution. The shift to the lower values was also reported by Saby et al. for benzoic acid covalently grafted to GC by electrochemical methods [51].

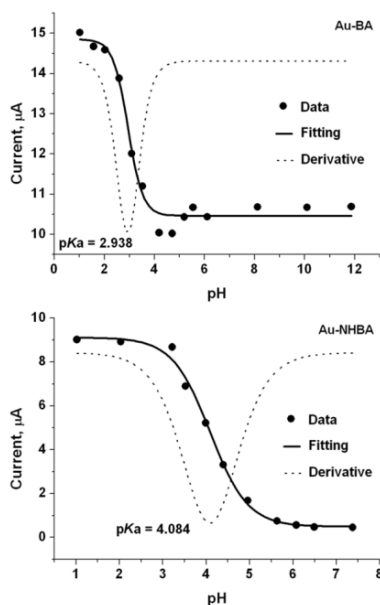


Figure 3. Cyclic voltammetric cathodic peak currents of Fe(CN)<sub>6</sub><sup>3-</sup> ions on Au-BA and Au-NHBA surfaces vs. pH of BR buffer solution in 0.1 M KCl.

### 3.3. pKa determination by electrochemical impedance spectroscopy

EIS is a powerful technique in determining the interfacial acid-base properties of the surface-modified electrodes. Therefore, to investigate the acid-base behavior the Au-BA and Au-NHBA modified surfaces, we also performed EIS experiments using 2 mM Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> redox couple at different pH values of BR buffer and measured the surface pKa values of the -BA and -NHBA films on Au electrode. Impedance properties of the surfaces due to the dissociation of the terminal -COOH groups of the -BA and -NHBA films exhibited pH dependence against redox probe, as explained above in the case of CV measurements. When the pH in buffer solution is higher than pKa of the surface (pH > pKa), the carboxylic acid groups on the -BA and -NHBA films dissociate and charge the surfaces negatively, creating repulsive forces between the surface and the negatively charged redox probe ions. On the contrary, at the lower pH conditions (pH < pKa), the surface confined -COOH groups are fully undissociated and in this case surface repulsive forces are not in action. As is observed in CV experiments, when the value of pH in Fe(CN)<sub>6</sub><sup>4-/3-</sup> solution is increased, we confirm the indicative transition in which the increase of negative charge on the modified surface lead to electrostatic repulsion between the probe and the electrode surface.

Impedance values are fitted to standard Randles equivalent circuit comprising of a parallel combination of a Warburg resistance and constant phase element (CPE) in the complete range of frequency. With the increase in the pH of the solution, the charge transfer resistance (R<sub>ct</sub>) value,

calculated from the impedance plot, increases due to the inhibition of the electron transfer rate of the redox probe (Figure 4). It means that the electrostatic repulsion of the redox probe increases with pH, due to the negatively charged surface. Figure 4 (a,b) shows the impedance plots on the Au-BA and Au-NHBA in Fe(CN)<sub>6</sub><sup>4-/3-</sup> redox couple solutions with various pHs. The diameter of the semicircle, which is a measure of R<sub>ct</sub>, increases impressively with the increase of pH of Fe(CN)<sub>6</sub><sup>4-/3-</sup> solution, due to inhibition of the charge transfer.

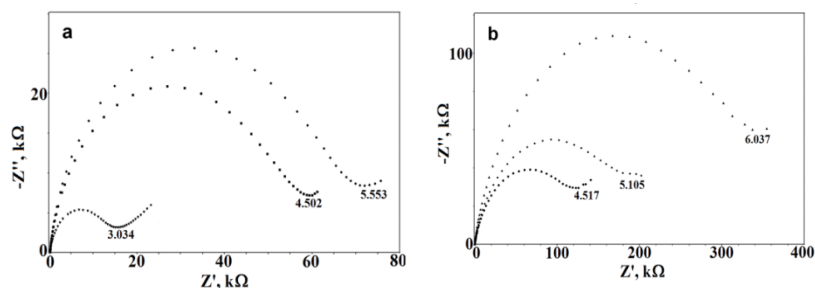


Figure 4. (a) Impedance plots on a Au-BA, (b) Au-NHBA in 2 mM Fe(CN)<sub>6</sub><sup>4-/3-</sup> in (BR) buffer solutions of different pHs (0.1 M KCl).

The R<sub>ct</sub> values calculated from impedance analysis in buffer solutions of different pHs are plotted against pH for Au-BA and Au-NHBA surfaces as shown in Figure 5 (a,b). The surface pK<sub>a</sub> of Au-BA and Au-NHBA films are measured from derivative curves of R<sub>ct</sub>/pH plots to about 4.128±0.342 and 5.326±0.443, respectively. The results of EIS measurements show that the pK<sub>a</sub> values of Au-BA surface is almost the same as that of benzoic acid in bulk solution. Conversely, pK<sub>a</sub> value shifted to higher values about 0.7 pK<sub>a</sub> unit for Au-NHBA compared to the pK<sub>a</sub> values in bulk solution. The shift to the higher values was also reported by Abiman et al. for benzoic acid grafted to graphitic powder surface [44,50,51].

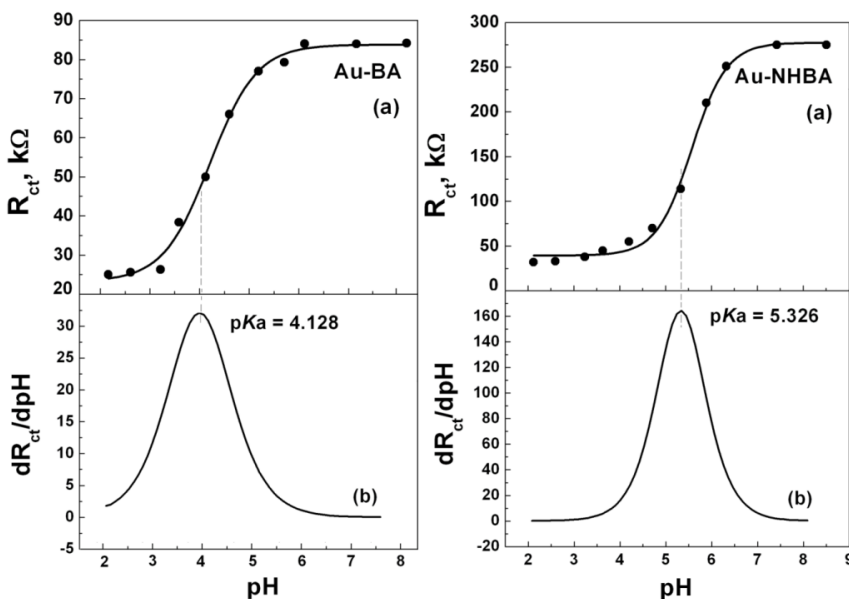


Figure 5. (a) Plots of charge-transfer resistance (R<sub>ct</sub>) as a function of solution pH for Au-BA and Au-NHBA surfaces, (b) derivative curves of R<sub>ct</sub> vs. pH plots.



### 3.4. pKa determination of benzoic acid modified gold electrode by contact angle measurement

Contact angle measurements are based on the consideration of a thermodynamic equilibrium between solid surfaces and the liquid phase [52,53]. Many properties of the surfaces can be retrieved by this method and the range of information obtained by CAM can be increased by measuring contact angles as a function of pH of aqueous drops and by examining both advancing and receding contact. Measurement procedure of contact angles against pH is called “contact angle titration” [54-57]. Like most techniques in physical-organic chemistry, measurement of contact angles relies heavily on comparisons of measurements in similar systems rather than on interpretation of absolute values [58,59].

pKa values of Au-BA and Au-NHBA surfaces were also investigated by contact angle titration (i.e. determination of contact angles as a function of pH), to confirm the accuracy of CV and EIS results. Contact angle titration of the surfaces produced sigmoidal plots of pH, as Figure 6a showed, for both Au-BA and Au-NHBA surfaces. As the  $-\text{COOH}$  groups of the Au-BA and Au-NHBA surfaces ionized with increasing pH, measured contact angles decreased due to the changes in the charge states of the surfaces. The surface pKa values for the Au-BA and Au-NHBA surfaces were detected as 4.251 and 5.102 respectively, from the inflection points of the  $\theta$ -pH plots or from the derivative of that curve, i.e. ( $d\theta/d\text{pH}$ ) versus pH (Figure 6b). It should be noted here that the pKa value of Au-BA film measured by CAM is the same with the pKa value of benzoic acid in the aqueous solution (4.20) [34,49,50], while it is 0.5 pKa unit larger in the case of p-aminobenzoic acid (4.60) [35,51].

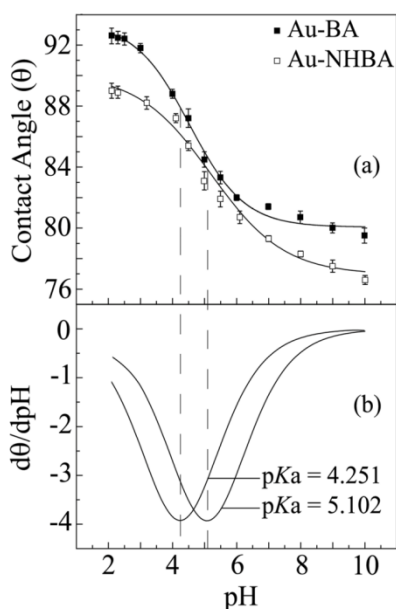


Figure 6. (a) Contact angle titration curves of Au-BA and Au-NHBA surfaces, (b) derivative curve of  $d\theta/d\text{pH}$  vs. pH.

### 3.5. Comparison of the surface pKa values of the modified gold electrodes acquired by CV, EIS and CAM techniques

The Table lists the pKa values of Au-BA and Au-NHBA surfaces determined by CV, EIS and CAM techniques. We observed that in the case of Au-BA surface, the pKa value was negatively shifted in CV measurements while no significant shifts were observed in EIS and CAM. For the Au-NHBA surface, the pKa value was still negatively shifted in CV, whereas it

was positively shifted both in EIS and CAM. When the pKa values of Au-BA and Au-NHBA surfaces are compared, the acidity of Au-NHBA surface is found to be weaker than that of Au-BA surface for all measurement techniques. The difference in surface acidity is more than 1 pKa unit while the bulk solution difference is 0.4 pKa unit. The reason for the pronounced decrease in Au-NHBA acidity can be attributed to the effect of substrate material which plays some role in changing the surface pKa values to some extent [43]. In a recent paper, Liu et al. extensively studied and reported the impact of the electrode material on the organic films grafted to the surfaces, where electron coupling between the metal electrode and the modifier molecules result to spill over the electron density into the organic film [24]. In gold substrate, the free electron pair of the -NH bridge are conjugated with the metallic electrons of the gold surface and enhancing the electron donating ability of the secondary amine group, which weaken the acidity of the surface confined -COOH protons. Thus, the conjugated electron cloud can be thought of as continuing into the -NHBA film more easily than into the -BA film.

The Table 1 also shows that the pKa values of Au-BA and Au-NHBA surfaces measured by CV are lower than that of bulk values in both case, but with a higher negative shift for the surface in which benzoic acid is grafted to Au through Au-C bond. The extent of shift is around -1.3 pKa unit for Au-BA and -0.5 for Au-NHBA reference to the pKa values of the same species in bulk solution. On the other hand, the average pKa values for Au-BA surface, found by EIS and CAM techniques showed no significant differences. In the case of Au-NHBA surface in which aminobenzoic acid is covalently grafted onto GC through the amine group, positive shifts are observed for both EIS and CAM techniques.

Table 1. pKa values of Au-BA and Au-NHBA surfaces determined by CV, EIS and CAM techniques and the shifts relative to the bulk solution pKa. ♣

Method	pKa of Au-BA	pKa of Au-NHBA	pKa shift for BA	pKa shift for p-ABA
CV	2.938±0.283♠	4.084 ±0.101	-1.3	-0.5
EIS	4.128±0.342	5.326±0.323	No significant shift	+0.7
CAM	4.251±0.089	5.102±0.147	No significant shift	+0.5

♣ In bulk solution pKa of BA is 4.20 [43,48,49] and p-aminobenzoic acid is 4.60 [35,50]

♠ Standard deviation for four measurements

The pKa values at Au for benzoic acid observed here are in good agreement with the literature values at the GC surface. The pKa value of benzoic acid covalently grafted to the glassy carbon surface has been reported by Abiman et.al. as 3.25[44] and by Saby et al as 2.8 [50]. On the other hand, Liu et al. reported that the pKa of p-aminobenzoic acid covalently grafted onto a GC electrode through the amine group is 3.0 [35]. These reported pKa values are all lower than for free species in solution although the shifts towards the higher pKa values have also been reported [44].

There are many factors that affect the surface pKa shifts, but the fundamental principles of these factors are not fully understood. Among them are the charge and hydrophobicity of the surface, lateral interactions between the adsorbed species, and the electronic interactions between surface confined species and the substrate. Usually, shifts are relatively small and generally less than 1 pKa unit. However, the shift more than about 3 pKa units has been reported for the 1-anthraquinoidal groups on the surface of graphitic powder and carbon nanotubes [44]. According to Baranton and Belanger, the most striking effect of pKa shift of benzoic acid is the confirmation of the -COOH group of the grafted layer, which decreases the pKa of the grafted film compared to that of the molecule in solution [48].

The substrate effect has been discussed in recent papers in detail comparing GC and Au. According to Liu et al. electronic coupling between the electrode material and the surface

adsorbed molecule is more effective in gold surfaces, as a consequence of wave function mixing [24]. This mixing is more effective in Au-NHBA, perhaps through the nonbonding electrons, shifting the pKa to the higher values. It is generally argued that the gold materials are more sensible than glassy carbon substrate in the case of electrostatic effect [24,44,48]. To be able to understand the reasons for the shift of the surface pKa values, a comprehensive study should be performed, considering the nature of the adsorbed species, the type of the substrate and the method of measurement as well.

#### 4. CONCLUSION

Gold surfaces were modified by electrochemical reduction of p-benzoic acid diazonium salt as well as electrochemical oxidation of p-aminobenzoic acid solutions. The film at the surface with ionizable carboxylic acid group imparted a barrier effect against the electrochemistry of Fe(CN)<sub>6</sub><sup>4-/3-</sup> redox probe, which was exploited to determine the pKa of the film at the gold surface. The pKa values of both surfaces were also evaluated by CAM in addition to the electrochemical methods. These pKa values were compared for two modified surfaces, i.e. Au-BA and Au-NHBA, and for the methods used in the measurements of acidities of the surface films. The sources of the negative and positive shifts of surface pKa values with respect to the pKa values of the same molecules in bulk solution were discussed. Among the three fundamentally different techniques, the most reliable ones are thought to be EIS and CAM, since the pKa measurements are performed in equilibrium conditions in these techniques. Although the electrochemistry of Fe(CN)<sub>6</sub><sup>4-/3-</sup> is reversible, the CV measurements is far from the thermodynamic equilibrium conditions in nature. The results of CAM and EIS measurements indicate that pKa value of the –COOH groups at the Au-BA surface is not significantly shifted relative to the solution value, while the shift for p-aminobenzoic acid is in the expected positive direction.

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