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Permeability of Alkanethiols Self-Assembled Monolayers on Gold Prepared by Neat Thiols and Ethanolic Thiols

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In this article we investigated the permeability of alkanethiols (C_nSH, n = 6, 10, 12, 16) self-assembled monolayers (SAMs) on gold prepared by neat thiols and ethanolic thiols. The electrochemical parameters (interfacial capacitance C_d, phase angle $\Phi_{1\,Hz}$ and ions transfer resistance R_{it}^* at 1 Hz, current density difference Δj and charge transfer resistance R_{ct}) from cyclic voltammetry (*CV*) and electrochemical impedance spectroscopy (*EIS*) were used to explore the permeability of SAMs. Results indicated that alkanethiols SAMs prepared by neat thiols had smaller C_d than by ethanolic thiols. Thus, the neat thiols SAMs were more compacted than ethanolic thiols SAMs. The dielectric constant ε of alkane chain in SAMs were calculated to be 1.2 (neat thiols) and 3.0 (ethanolic thiols) respectively based on the linear slopes of C_d^{-1}~n plots. A hydrophobic gap possibly existed on neat thiols SAMs-water interface, which might lead to smaller ε (1.2) than the reported value (2.3) by literatures. The $\Phi_{1\,Hz}$ of neat thiols SAMs were bigger and close to 88° as an ions insulator and the ethanolic thiols SAMs were ions permeable SAMs. The permeable constants (p) of neat thiols SAMs and ethanolic thiols SAMs on gold were 0.097/CH_2 and 0.111/CH_2 respectively based on the linear slopes of lnR_{it}^* ~ n plots. However, to our surprise, the tunneling constant β of neat thiols SAMs was calculated to be 0.238/CH_2 based on the linear slopes of lnR_{ct} ~ n plots (R_{ct} was the charge transfer resistance of $Fe(CN)_6^{3-/4-}$), which was much smaller than 1.0/CH_2 from literatures. We considered that there might be two main reasons: 1) The hydrophobic layer existed on the neat thiols SAMs possibly influenced the R_{ct} of $Fe(CN)_6^{3-/4-}$; 2) The neat thiols SAMs was not an ideal tunneling system with the collapsed sites possibly existed in SAMs, which might influence the R_{ct} of $Fe(CN)_6^{3-/4-}$. These conclusions provided the important reference for understanding the interfacial characteristics of alkanethiols SAMs on gold in depth.

Keywords: self-assembled monolayers, permeability, neat thiols, ethanolic thiols, gold electrode

1. INTRODUCTION

Self-assembled monolayers (SAMs) adsorbed on solid substrate are being intensively studied for their wide application in some research fields, such as wetting, biosensing, adhesion, and corrosion[1,2]. Alkanethiols SAMs adsorbed on gold substrate are usually applied due to the strong covalent interaction between thiols and gold [3,4]. The ions permeability and electron transfer performance through thiols SAMs are concerned by researchers. Defects or collapsed sites possibly exist in thiols SAMs on gold, which might influence the ions permeability and electron transfer performance in SAMs. How to prepare compacted, defect-free, and collapsed site-free thiols SAMs on gold is the key problem.

Many methods have been proposed for preparing the high-quality alkanethiols SAMs on gold, such as microwave irradiation [5], ultrasonic irradiation [6], magnetic field[7], potential control[8], specific solvents (ionic liquid, micellar solution, hexagonal lyotropic liquid crystalline phase)[9−11], and neat thiols [12−14] for assembly. Among these, it is beneficial for using neat thiols (without solvent) to assemble alkanethiols SAMs because solvent might permeate into SAMs, dissolve the alkane chain of alkanethiols, and make thiols SAMs disordered [12−14]. However, the alkanethiol SAMs prepared by neat thiols show an unusually low interfacial capacitance C_d, which is much smaller than the theoretical C_d value [12,13]. Lakshminarayanan and Sampath et al proposed that a hydrophobic gap might be existed at the alkanethiols SAM–water interface, which possibly decreased the C_d of the total alkanethiols SAMs [12,13]. Also some experimental and simulational results indicated that water at hydrophobic substrates had reduced density or formed a vacuum layer with a few angstrom thickness [15−17]. Based on the above reports, we focus on the two problems unsolved: 2) How the thickness of the hydrophobic gap is; 2) how the hydrophobic gap influences the permeability (ions permeation and electron transfer) through alkanethiols SAMs.

In order to explore the above two problems, in the article we systematically investigate the ions permeability and electron transfer performance of the alkanethiols SAMs (C_nSH, n = 6, 10, 12, 16) prepared by neat thiols and ethanolic thiols through cyclic voltammetry (*CV*) and electrochemical impedance spectroscopy (*EIS*). The relationships of electrochemical parameters related to ions permeation and electron transfer with n of C_nSH are explored fully combined with literature reports.

2. EXPERIMENTAL SECTION

2.1 Chemicals and apparatus

1-Hexanethiol (C_6SH, ≥97%, Alfa), 1-Decanethiol ($C_{10}SH$, ≥96%, Aldrich), 1-Dodecanethiol ($C_{12}SH$, ≥98%, Aldrich), 1-Hexadecanethiol ($C_{16}SH$, ≥97%, Alfa). Sodium sulfate anhydrous (Na_2SO_4, ≥99.8%), absolute ethanol (≥99.8%), potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$, ≥99.5%), potassium ferrocyanide trihydrate ($K_4Fe(CN)_6{\cdot}3H_2O$, ≥99.5%) were from Shanghai Sinopharm Chemical Reagent Company Ltd. All chemicals were analytical grade and used as received. Ultrapure water (18 MΩ•cm) was used in all experiments. The CHI660D electrochemical workstation (CH

Instruments, USA) was used for *CV* and *EIS* experiments. Electrochemical cell included a three-electrode system: working electrode (polycrystalline gold, 2 mm diameter, CH Instruments), counter electrode (platinum electrode) and reference electrode (saturated calomel electrode, SCE). Solutions were deaerated with high-purity N_2.

2.2. Pretreatment of gold electrodes

The planar gold electrodes were pretreated based on our previously reported procedure [18]. Firstly the gold electrodes were hand-polished on microcloth pads with alumina slurries (1.0, 0.3 and 0.05 µm), sonicated in ultrapure water for 10 min, then dipped into newly prepared diluted aqua regia solution (H_2O: HCl: HNO_3 = 6:3:1 by volume) for 5 min, finally sonicated in ultrapure water for 15 min. Then the gold electrodes were scaned in 0.5 M H_2SO_4 solution from −0.4 to +1.5 V at 0.1 V s^{-1} to obtain reproducible *CV* plots. The real surface area A of gold electrodes was determined by *Q*/400, where *Q* was the integrated charge of reduction peak for gold oxide, 400 was the theoretical reduction charge of gold oxide each unit area (µC cm^{-2}).

2.3. Preparement of alkanethiols SAMs on gold

The pretreated gold electrodes were dipped into neat thiols or ethanolic thiols (C_nSH, n = 6, 10, 12, 16) to assemble for 48 h. Then the gold electrodes were removed out, rinsed with absolute ethanol and ultrapure water in turn, put into the electrochemical cell for experiment.

2.4. Electrochemical measurement

2.4.1 Interfacial capacitance (C_d)

C_d was measured by *CV* in 0.1 M Na_2SO_4 solution at different scan rate v (0.1, 1, 5, 20, 50 V s^{-1}) with potential window from −0.2 to +0.2 V. The equation was $C_d = i/2vA$ where i was the summed current (µA) from the positive and negative scan directions at 0 V, v was the scan rate (V s^{-1}) and A was the real area of gold electrode (cm^2)[19].

2.4.2 The absolute value of phase angle (Φ_{1Hz}) and ions transfer resistance (R_{it}^*) at 1 Hz

The absolute value of phase angle (Φ_{1Hz}) and ions transfer resistance (R_{it}^*) at 1 Hz were used to investigate the ions permeability in SAMs. The compacted alkanethiols SAMs had bigger Φ_{1Hz} and R_{it}^* values than the sparse alkanethiols SAMs. The Φ_{1Hz} and R_{it}^* were measured by *EIS* in 0.1 M Na_2SO_4 solution with the potential fixed at 0 V, the frequency ranged from 0.1 Hz to 10^5 Hz and the amplitude for 5 mV[19].

2.4.3 Current density difference (Δj) and charge transfer resistance (R_{ct})

Δj and R_{ct} were measured in 2 mM $K_3Fe(CN)_6$ and 0.1 M Na_2SO_4 solutions by *CV* and *EIS*. For *CV* measurement, the potential window of *CV* was from −0.2 to +0.5 V and the scan rate was 0.1 V s^{-1}. Δj was the current density difference of $Fe(CN)_6^{3-}$ at −0.2 V and +0.5 V ($\Delta j = \left| j_{-0.2\text{V}} - j_{+0.5\text{V}} \right|$). For *EIS* measurement, the potential was fixed to the formal potential, the frequency was from 0.1 Hz to 10^5 Hz, and the amplitude was 5 mV [19]. Randle equivalent circuit (*RQR*) was used to simulate the *EIS* plots, which were shown in Figure 1. The R_s was the uncompensated solution resistance, the *Q* was constant phase element (*CPE*), and the R_{ct} was charge transfer resistance.

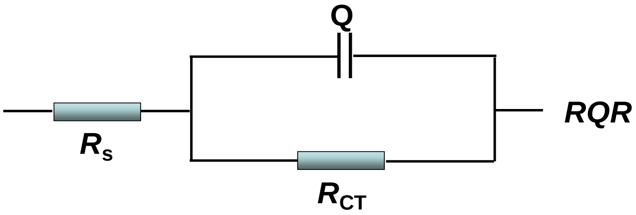


Figure 1. The equivalent circuits (*RQR*) for simulating *EIS* plots.

3. RESULTS AND DISCUSSION

3.1 Comparison of ions permeability in SAMs on gold prepared by neat thiols and ethanolic thiols

3.1.1 Interfacial capacitance C_d

Figure 2A and 2B showed the *CV* plots of alkanethiols (C_nSH, n = 6, 10, 12, 16) SAMs on gold prepared by neat thiols or ethanolic thiols in 0.1 M Na_2SO_4 solution at 0.1 V s^{-1}. The *CV* charging current became smaller and smaller with the increasing alkane chain length of thiols. Furthermore, the *CV* charging current of C_nSH SAMs prepared by neat thiols was smaller than by ethanolic thiols. Based on $C_d = i/2vA$, we obtained the C_d values of C_nSH SAMs on gold, which were shown in Figure 2C, Figure 2D and Table 1. The C_d values of C_nSH SAMs prepared by neat thiols were smaller than by ethanolic thiols. Along with the increase of *CV* scan rate, the C_d values of C_nSH SAMs prepared by neat thiols were almost constant, which reflected that ions were hard to permeable into the SAMs. On the contrary, the C_d values of C_nSH SAMs prepared by ethanolic thiols decreased with increasing *CV* scan rate, which indicated that ions could permeable into the SAMs. These above experimental results indicated that C_nSH SAMs prepared by neat thiols were more compacted than by ethanolic thiols.

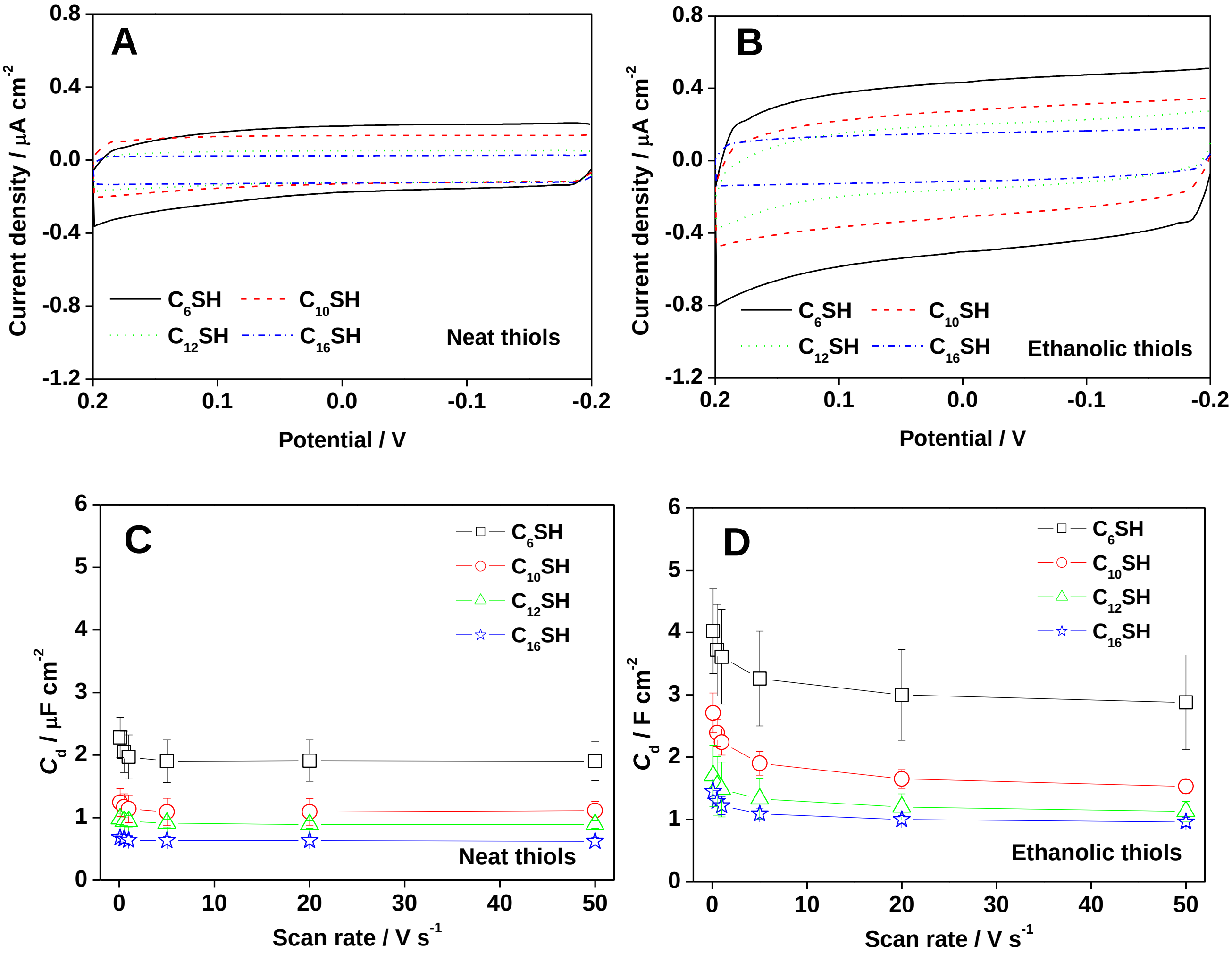
The C_d value of C_nSH SAMs calculated at low *v* by *CV* was bigger than that at high *v*, which could reflect ions permeability in SAMs more. According to the C_d values of C_nSH SAMs obtained by *CV* at the scan rate of 0.1 V s^{-1}, we drew the plots of C_d^{-1}~ n, as Figure 2E and 2F showed. The plots of C_d^{-1}~ n were linear for C_nSH SAMs prepared by neat thiols or ethanolic thiols. The linear equations were:

$C_d^{-1} = -0.154 + 0.100\,n$ ($R^2 = 0.9987$, neat thiols)

$C_d^{-1} = -0.013 + 0.041$ n ($R^2 = 0.9263$, ethanolic thiols)

The C_d of C_nSH SAMs might be calculated by $C_d = \varepsilon\varepsilon_o/d$, where ε_o was the permittivity of free space (8.85×10^{-14}F cm^{-1}), ε was the dielectric constant of C_nSH SAMs and d was SAMs' thickness (Å) [20]. Because d was equal to 1.1 n + 2.5 Å (considering 30^o tilted angle of alkanethiols SAMs) [21], the plots of C_d^{-1} with n might be linear with the slopes of $1.1/\varepsilon\varepsilon_o$. Based on the slopes of C_d^{-1}~n plots, we obtained that ε of alkane chain in SAMs were 1.2 (neat thiols) and 3.0 (ethanolic thiols).

The ε of alkane chain in alkanethiols SAMs reported by literatures was 2.3[22], which was different from our experimental results. For thiols SAMs prepared by us with ethanolic thiols, the ε was bigger than 2.3. We considered that the collapsed sites or defects might exist in the thiols SAMs, which availed the permeation of water and ions in SAMs and led to the increase of dielectric constant in SAMs. For thiols SAMs prepared by us with neat thiols, the ε was much smaller than 2.3, which was possibly due to the existence of hydrophobic gap on thiols SAMs-water interface[12,13,23].



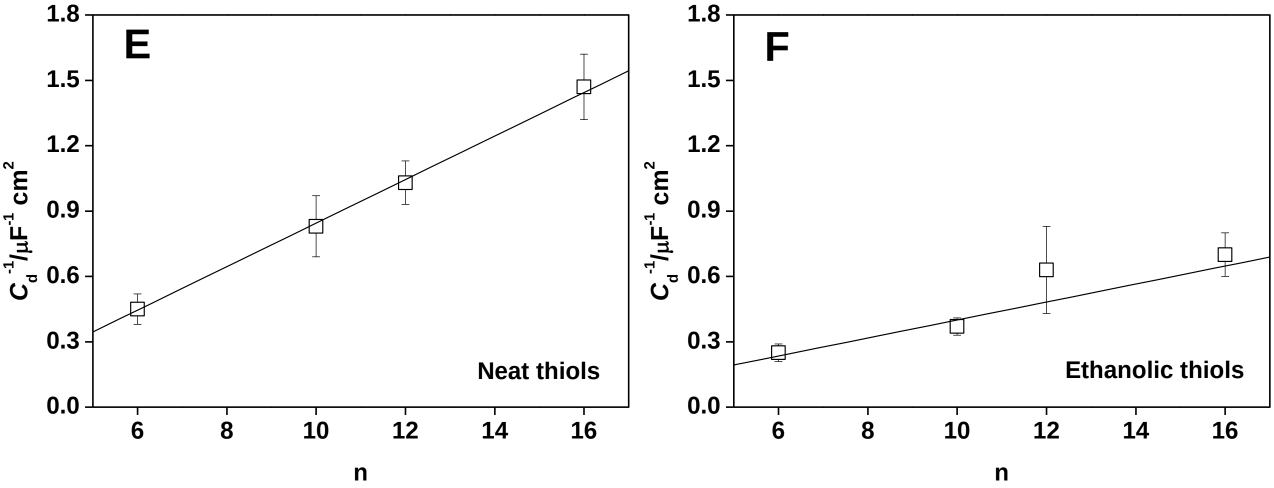


Figure 2. (A, B) *CV* plots of alkanethiols (C_nSH, n = 6, 10, 12, 16) SAMs on gold in 0.1 M Na_2SO_4 solution at 0.1 V s^{-1}. (C, D) Relationships of C_d of alkanethiols SAMs on gold with scan rate *v*. The C_d values were calculated by *CV* plots at different scan rate *v* with potential scan window from −0.2 V to 0.2 V. (E, F) Relationships of C_d^{-1} obtained by *CV* at 0.1 V s^{-1} with n of alkanethiols (C_nSH). The alkanethiols SAMs on gold were prepared by dipping into neat thiols or ethanolic thiols for self-assembly.

Supposed that the total interface of thiols SAMs prepared by neat thiols included two capacitors in series:

$$\frac{1}{C_d} = \frac{1}{C_{d(thiols)}} + \frac{1}{C_{d(layer)}}$$

Where C_d was the capacitance of thiols SAMs, $C_{d(thiols)}$ was the capacitance of thiols layer and $C_{d(layer)}$ was the capacitance of hydrophobic layer. Due to the linear relationships of C_d^{-1}~n and $C_{d(thiols)}^{-1}$~n proved by the results from our experiment and literature report, the plot of $C_{d(layer)}^{-1}$ ~ n might be linear. If $C_{d(layer)}$ was equal to $\varepsilon_{(layer)}\varepsilon_o/d_{(layer)}$ and $\varepsilon_{(layer)}$ was a constant value, then the thickness $d_{(layer)}$ of hydrophobic gap would be bigger and bigger with the increase of alkane chain length of thiols.

Compared the C_d data in our work with literature reports (see in Table 1), it was found that most of C_d data were consistent [5, 9, 14, 23, 24]. However, there were also some different data. Lakshminarayanan and Subramanian et al [12,13] reported the C_d values of neat thiols SAMs (1.2, 0.55, 0.35 and 0.29 μF cm^{-2} for neat C_6SH, $C_{10}SH$, $C_{12}SH$ and $C_{16}SH$ respectively), which were smaller than our experimental values (see in Table 1). This indicatd that neat thiols SAMs prepared by Lakshminarayanan and Subramanian might be more compacted than those prepared by us. Based on the C_d values reported by Lakshminarayanan and Subramanian et al [12,13], we drew the plot of C_d^{-1}~ n. The plots of C_d^{-1}~ n were linear with linear equation as:

$C_d^{-1} = -0.746 + 0.271$ n ($R^2 = 0.9583$, neat thiols)

Based on the slopes of C_d^{-1}~n, we obtained that *ε* of alkane chain in neat thiols SAMs was 0.46. This also proved that the hydrophobic layer might be existed on the neat thiols SAMs and the thickness $d_{(layer)}$ of hydrophobic layer was bigger for neat thiols SAMs with longer alkane chains.

3.1.2 Phase angle Φ_{1Hz} and ions transfer resistance R_{it}^{*}

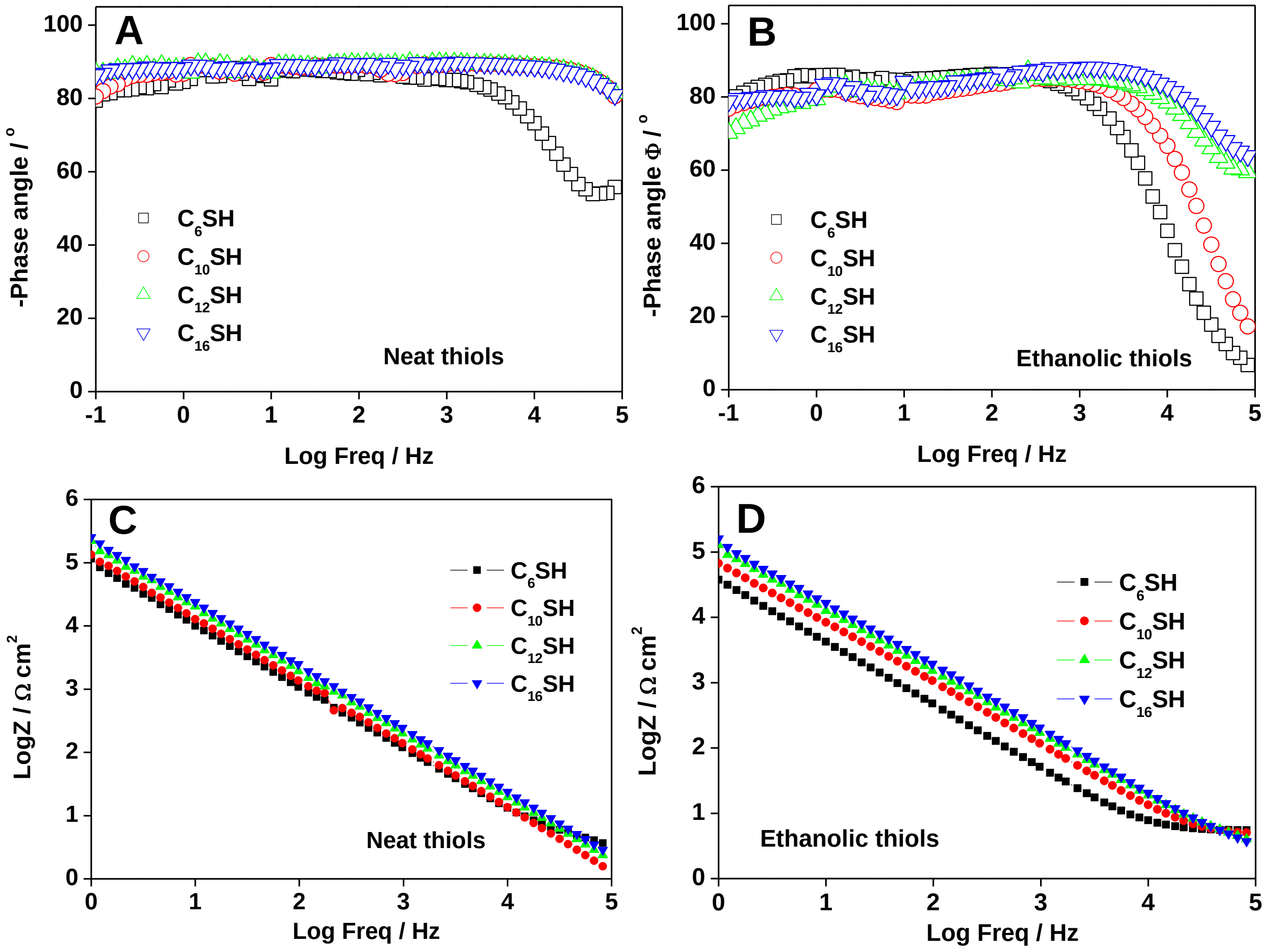
Figure 3A, 3B, 3C and 3D showed the *EIS* plots of alkanethiols (C_nSH, n = 6, 10, 12, 16) SAMs on gold prepared by neat thiols or ethanolic thiols in 0.1 M Na_2SO_4 solution. Because the phase angle and resistance at lower frequency could reflect the ions permeability in SAMs, we mainly investigated the data of phase angle and resistance at 1 Hz (Φ_{1Hz} and R_{it}*), which were included in Figure 3E, Figure 3F and Table 1. For thiols SAMs prepared in neat thiols, Φ_{1Hz} was about 88° and independent of alkane chain length, indicating that thiols SAMs prepared in neat thiols were ions insulator, consistent with the reports from literatures (see in Table 1)[5,6,9,11,12,14]. For thiols SAMs prepared in ethanolic thiols, Φ_{1Hz} was smaller than 88°, which indicated that ions could permeable into thiols SAMs. Samely the R_{it}* was always bigger for neat thiols SAMs than ethanolic thiols SAMs. The results indicated that the neat thiols SAMs was more compacted than ethanolic thiols SAMs.

The plots of $\ln R_{it}^{*} \sim$ n were linear and the linear equations were:

$\ln R_{it}^{*} = 10.792 + 0.107\ n$ ($R^2 = 0.9916$, neat thiols)

$\ln R_{it}^{*} = 9.992 + 0.122\ n$ ($R^2 = 0.9618$, ethanolic thiols)

Supposing that $\ln R_{it}^{*} = k + pd$, p was the permeable constant, k was the constant and d was the thickness of SAMs ($d = 1.1n + 2.5$ Å), we obtained that the p was 0.097/CH_2 and 0.111/CH_2 for thiols SAMs prepared in neat thiols and ethanolic thiols respectively.



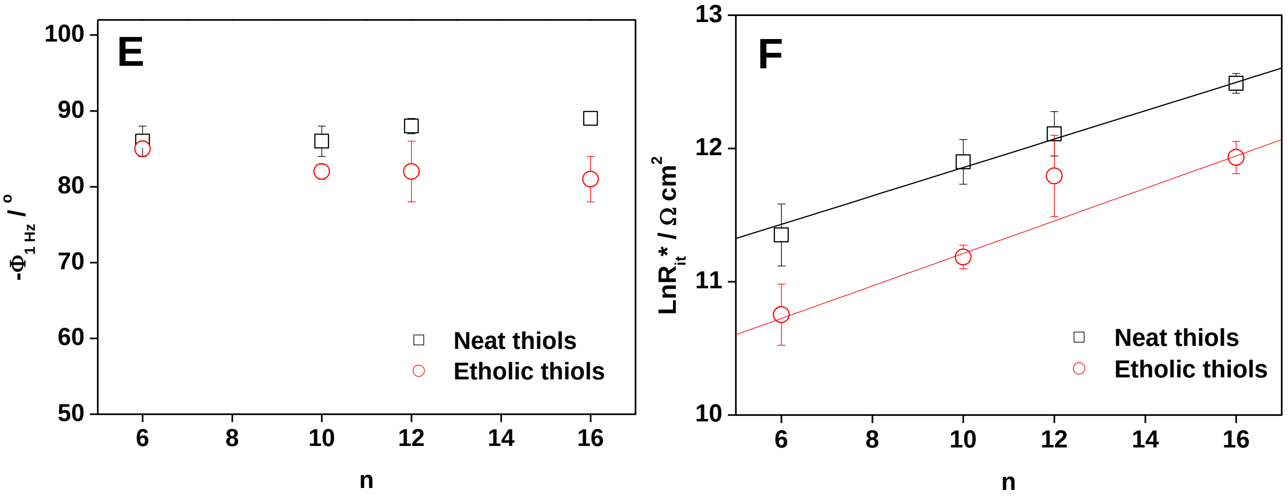


Figure 3. (A, B) The plots of phase angle Φ with frequency and (C, D) the total impedance resistance (logZ) with frequency for alkanethiols (C_nSH, n = 6, 10, 12, 16) SAMs on gold in 0.1 M Na_2SO_4 solution. (E, F) Relationships of phase angle at 1 Hz (Φ_{1Hz}) or ion transfer resistance (R_{it}) at 1 Hz with n of alkanethiols (C_nSH). The alkanethiols SAMs on gold were prepared by dipping into neat thiols or ethanolic thiols for self-assembly.

3.2 Comparison of electron transfer performance through SAMs on gold prepared by neat thiols and ethanolic thiols

Figure 4A, 4B, 4C and 4D showed the *CV* and *EIS* plots of alkanethiols (C_nSH, n = 6, 10, 12, 16) SAMs on gold prepared by neat thiols or ethanolic thiols in 2 mM $Fe(CN)_6^{3-/4-}$ and 0.1 M Na_2SO_4 solution. Based on the *CV* and *EIS* plots, we calculated the Δj and R_{ct} of $Fe(CN)_6^{3-/4-}$ through thiols SAMs on gold (see in Table 1). The plots of Δj~n and $\log R_{ct}$~n were showed in Figure 4E and 4F. The Δj was smaller and R_{ct} was bigger for thiols SAMs prepared by neat thiols than ethanolic thiols, indicating that thiols SAMs prepared by neat thiols were more compacted than by ethanolic thiols.

For neat thiols SAMs on gold, the linear relationships of $\log \Delta j$ ~ n and $\log R_{ct}$ ~ n were good with the linear equations as:

$\ln\Delta j = 2.810 - 0.287$ n ($R^2 = 0.9590$, neat thiols)

$\ln R_{ct} = 12.375 + 0.262$ n ($R^2 = 0.9831$, neat thiols)

Literatures reported that electron transfer mechanism through the compacted and defect-free alkanethiols SAMs was mainly a tunneling process [25,26]. The tunneling equation was:

$$\ln \Delta j = \ln \Delta j_o - \beta d$$

$$\ln R_{ct} = \ln R_o + \beta d$$

Where Δj or R_o was the pre-exponential factor, β was the tunneling constant and d was the average distance of redox probes with gold surface. Based on the slopes of $\ln\Delta j$ ~ n and $\ln R_{ct}$ ~ n plots and the equation $d = 1.1\ n + 2.5$ Å, we obtained that β was 0.261/CH_2 and 0.238/CH_2 respectively. However, the β values reported by us were smaller than literature reported value 1.0/CH_2.

For ethanolic thiols SAMs on gold, the linear relationships of $\log \Delta j$ ~ n and $\log R_{ct}$ ~ n were worse with the linear equations as:

$\ln\Delta j = 6.651 - 0.495\ n\ (R^2 = 0.7508$, ethanolic thiols)

$\ln R_{ct} = 6.874 + 0.578\ n\ (R^2 = 0.9008$, neat thiols)

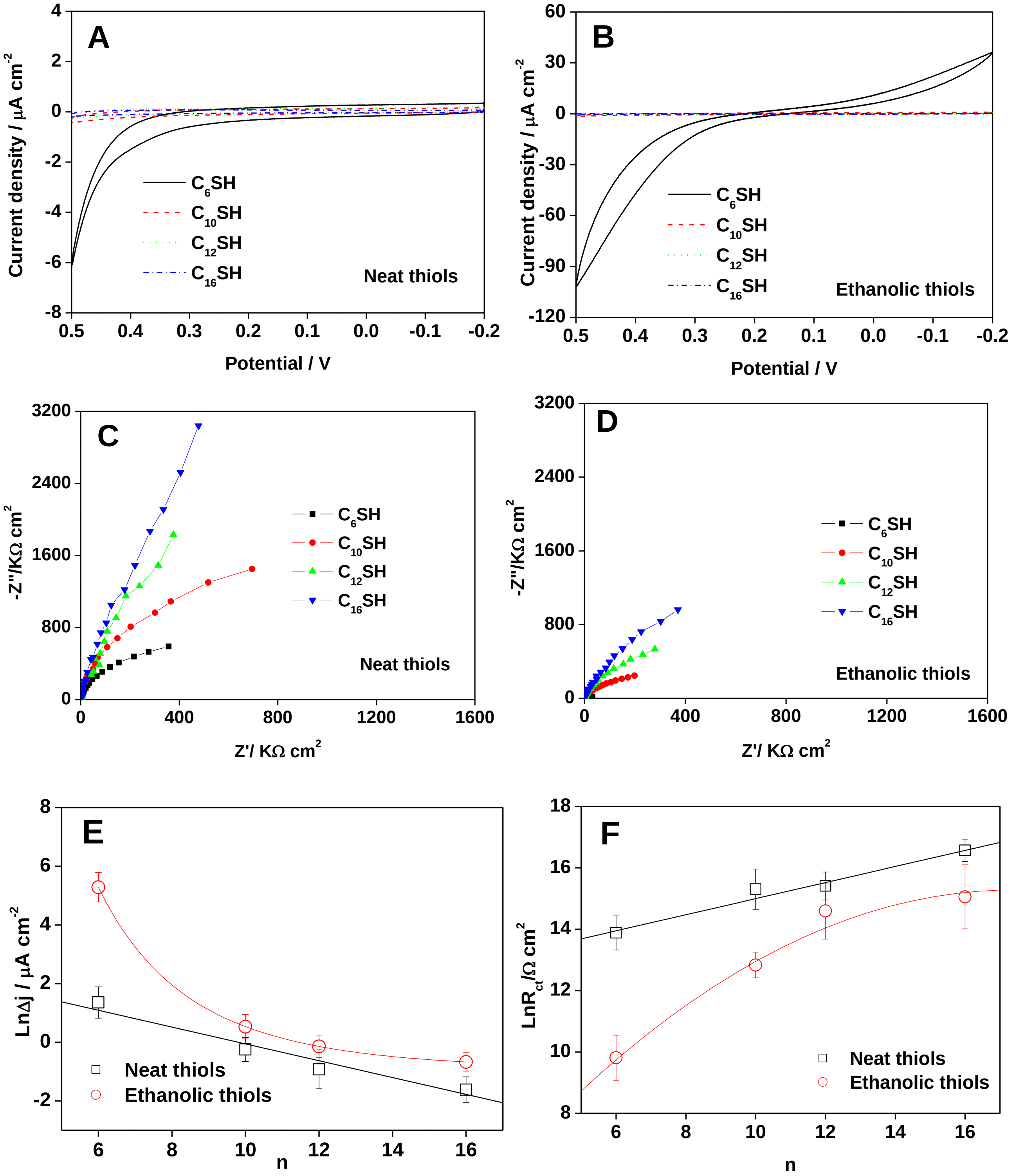


Figure 4. (A, B) *CV* plots and (C, D) *EIS* plots of alkanethiols (C_nSH, n = 6, 10, 12, 16) SAMs on gold in 2 mM $Fe(CN)_6^{3-}$ and 0.1 M Na_2SO_4 solution. The *CV* plots were scaned at 0.1 V s^{-1}. (E, F) Relationships of $\ln\Delta j$ and $\ln R_{ct}$ with n of alkanethiols (C_nSH). The alkanethiols SAMs on gold were prepared by dipping into neat thiols or ethanolic thiols for self-assembly.

Considering that ethanolic thiols SAMs had bigger C_d values and smaller Φ_{1Hz} and R_{it}*, then electron transfer through ethanolic thiols SAMs might not be only a tunneling process and other electron transfer paths should be existed (e.g., electron transfer through the collapsed sites or defects in SAMs).

Table 1 Electrochemical parameters of alkanethiols SAMs on gold prepared by neat thiols and ethanolic thiols

Thiols	Ions permeability								$Fe(CN)_6^{3-/4-}$ electron transfer	
	CV						*EIS*		*CV*	*EIS*
	C_d (μF cm^{-2})						$\Phi_{1\ Hz}$ (^{o})	R_{it}* (10^5 Ω cm^2)	Δj (μA cm^{-2})	R_{ct} (10^5Ω cm^2)
	0.1 V s^{-1}	0.5 V s^{-1}	1 V s^{-1}	5 V s^{-1}	20 V s^{-1}	50 V s^{-1}				
(a)Neat C_6SH	2.28 ± 0.32	2.05 ± 0.33	1.97 ± 0.35	1.90 ± 0.34	1.91 ± 0.33	1.90 ± 0.31	86 ± 2	0.87 ± 0.20	4.27 ± 1.86	11.8 ± 5.2
(a)Neat $C_{10}SH$	1.24 ± 0.22	1.17 ± 0.21	1.14 ± 0.22	1.09 ± 0.22	1.09 ± 0.21	1.11 ± 0.15	86 ± 2	1.49 ± 0.24	0.83 ± 0.30	51.2 ± 25.5
(a)Neat $C_{12}SH$	0.98 ± 0.09	0.94 ± 0.07	0.94 ± 0.09	0.91 ± 0.06	0.89 ± 0.06	0.89 ± 0.06	88 ± 1	1.83 ± 0.32	0.45 ± 0.25	52.6 ± 21.4
(a)Neat $C_{16}SH$	0.68 ± 0.07	0.66 ± 0.07	0.64 ± 0.08	0.63 ± 0.07	0.63 ± 0.05	0.62 ± 0.06	89 ± 0	2.66 ± 0.20	0.21 ± 0.08	165.6 ± 58.9
(a)Ethanolic C_6SH	4.02 ± 0.68	3.72 ± 0.74	3.61 ± 0.76	3.26 ± 0.76	3.00 ± 0.73	2.88 ± 0.76	85 ± 1	0.48 ± 0.11	210 ± 102	0.2 ± 0.1
(a)Ethanolic $C_{10}SH$	2.71 ± 0.32	2.39 ± 0.22	2.24 ± 0.21	1.90 ± 0.19	1.65 ± 0.15	1.53 ± 0.11	82 ± 1	0.74 ± 0.09	1.78 ± 0.72	3.9 ± 1.6
(a)Ethanolic $C_{12}SH$	1.70 ± 0.49	1.54 ± 0.47	1.48 ± 0.44	1.33 ± 0.33	1.20 ± 0.21	1.13 ± 0.16	82 ± 4	1.37 ± 0.42	0.91 ± 0.36	29.4 ± 28.5
(a)Ethanolic $C_{16}SH$	1.45 ± 0.20	1.29 ± 0.17	1.22 ± 0.14	1.09 ± 0.08	1.00 ± 0.06	0.96 ± 0.07	81 ± 3	1.53 ± 0.18	0.53 ± 0.15	54.0 ± 62.5
(b)Neat C_6SH	1.2 [13]									
(b)Neat $C_{10}SH$	0.55[12]									
(b)Neat $C_{12}SH$	0.35[12], 1.22 [14]		1.19[14]	1.10[14]	1.09[14]	1.09[14]	88.6[14]		0.71[14]	23.2[14]
(b)Neat $C_{16}SH$	0.29[12]						88[12]			
(b)Ethanolic C_6SH	3.5 ± 0.3[13]									
(b)Ethanolic $C_{10}SH$							84[11]			0.35[29]
(b)Ethanolic $C_{12}SH$	1.71[5,6,9,14]	1.36[5,6,9,14]	1.25[5,6,9,14]	1.19[5,6,9,14]	1.17[5,6,9,14]	0.97[5,6,9,14]	88[5,6,9,14]		0.97[5,6,9,14]	10.4[5,6,9,14]
(b)Ethanolic $C_{16}SH$	1.40[23], 1.42[12]						86[11]			18.0[30]
(c)C_6SH	2.24									0.02
(c)$C_{10}SH$	1.51									1.1
(c)$C_{12}SH$	1.30									8.3
(c)$C_{16}SH$	1.01									454.8

(a) Experimental values by us (the mean value and standard deviation of triplicate measurements, n=3).

(b) Literature reported values: (1) neat thiols: assembly time, 1 h [12]; 2 h [13]; 24 h [14]. (2) Ethanolic thiols: assembly time, 12 h[13]; 15 h [11]; 16 h[29]; 24 h[5,6,9,12,14,23]; 100 h[30]. Concentration of thiols, 1 mM [11,12,23,29,30]; 3 mM[13]; 10 mM[5,6,9,14].

(c) Theoretical values: (1) C_d: C_d was calculated by $C_d = \varepsilon\varepsilon_o/d$[20], where ε_o was the permittivity of free space (8.85×10^{-14}F cm^{-1}), ε was the dielectric constant 2.3 of C_nSH SAMs and d was SAMs' thickness, which was equal to 1.1 n + 2.5 Å by supposing 30^o tilted angle of thiols SAMs. (2) R_{ct}: The electron transfer rate k_o of $Fe(CN)_6^{3-/4-}$ on bare gold was supposed to be 0.026 cm s^{-1} [28]

and the tunneling constant β was $1.0/CH_2$[26,27]. Based on $k_{app} = k_o e^{-\beta d}$ and $k_{app} = RT/n^2F^2R_{ct}C$ [11] (k_{app} was the apparent rate constant, R_{ct} was the charge transfer resistance, C was the concentration of 2 mM $Fe(CN)_6^{3-/4-}$), we could calculate the theoretical R_{ct} of $Fe(CN)_6^{3-/4-}$ through thiols SAMs.

3.3 Possible reasons arousing the difference of ions permeability and electron transfer performance

Based on the above experimental data, we obtained the following conclusions: 1) Neat thiols SAMs were more compacted than ethanolic thiols SAMs. The neat thiols SAMs were approximate to an ions insulator and the hydrophobic layer might be existed at the neat thiols SAM/water interface. The ethanolic thiols SAMs were ions permeable monolayers and collapsed sites or defects might be existed in SAMs; 2) The permeable constant p was $0.097/CH_2$ and $0.111/CH_2$ for neat thiols SAMs and ethanolic thiols SAMs respectively; 3) The tunneling constant β was $0.238/CH_2$ for neat thiols SAMs.

For permeable constant p, the p value for neat thiols SAMs was smaller than that for ethanolic thiols SAMs. This conclusion was consistent with our anticipation. When n of C_nSH was smaller, the R_{it}* should be much smaller for ethanolic thiols SAMs than neat thiols SAMs because ethanol might easily interfere with the order of short-chian thiols SAMs. When n of C_nSH was bigger, the R_{it}* should be close to each other for ethanolic thiols SAMs and neat thiols SAMs because the strong Van der Waals force between adjacent long-chian thiols might hinder the entrance of ethanol in SAMs and reduce the interference on the order of thiols SAMs. Thus, the linear slope of $\ln R_{it}^*\sim n$ should be bigger for ethanolic thiols SAMs than neat thiols SAMs and the p value for neat thiols SAMs would be smaller.

For the tunneling constant β, the reports from literatures were $1.0/CH_2$ [26,27]. Based on $k_{app} = k_o e^{-\beta d}$ and $k_{app} = RT/n^2F^2R_{ct}C$ [11], we might calculate the theoretical R_{ct} of $Fe(CN)_6^{3-/4-}$ through thiols SAMs. The k_{app} was the apparent rate constant of $Fe(CN)_6^{3-/4-}$ through thiols SAMs, R_{ct} was the charge transfer resistance, C was the concentration of $Fe(CN)_6^{3-/4-}$ (2 mM), and k_o was the electron transfer rate of $Fe(CN)_6^{3-/4-}$ on bare gold, which was supposed to be 0.026 cm s^{-1}[28]. The theoretical R_{ct} of $Fe(CN)_6^{3-/4-}$ through C_nSH (n = 6, 10, 12, 16) SAMs was calculated to be 0.02, 1.1, 8.3 and 454.8 MΩ cm^2 respectively, which differed from our experimental values (11.8, 51.2, 52.6 and 165.6 MΩ cm^2 for neat thiols SAMs; 0.2, 3.9, 29.4 and 54.0 MΩ cm^2 for ethanolic thiols SAMs). The experimental R_{ct} of $Fe(CN)_6^{3-/4-}$ was bigger for C_nSH (n = 6,10,12) and smaller for C_nSH (n = 16). Furthermore, compared with the R_{ct} from our experiment and literature reports (see in Table 1)[14,24,29,30], it was found that R_{ct} from our experiment were bigger than most of reports from literatures, indicating that alkanethiols SAMs prepared by us were more compacted.

We considered that the difference of β from our experiment ($0.238/CH_2$) and literature report ($1.0/CH_2$) might be due to the following two reasons: 1) The hydrophobic layer with different thickness might be existed on the neat C_nSH (n = 6, 10, 12, 16) SAMs, which possibly influenced the R_{ct} of $Fe(CN)_6^{3-/4-}$. 2) Although neat thiols SAMs were like an ions insulator (e.g., C_d was independent of scan rate v and Φ_{1Hz} was about 88^o), it might not be an ideal tunneling system in our experiment with the collapsed sites possibly existed in SAMs[31,32], which might reduced the R_{ct} of $Fe(CN)_6^{3-/4-}$.

4. CONCLUSIONS

Permeability of alkanethiols SAMs on gold prepared by neat thiols and ethanolic thiols was investigated by *CV* and *EIS* methods. The order and compactness of neat thiols SAMs were much better than ethanolic thiols SAMs. The neat thiols SAMs had smaller C_d and Δj, bigger Φ_{1Hz}, R_{it}^* and R_{ct}. The dielectric constant ε of alkane chain in neat thiols SAMs was 1.2, smaller than 3.0 in ethanolic thiols SAMs and 2.3 from literature reports. A hydrophobic gap possibly existed on neat thiols SAMs-water interface, which might lead to smaller ε. The permeable constants p of neat thiols SAMs and ethanolic thiols SAMs on gold were 0.097/CH_2 and 0.111/CH_2 respectively. The tunneling constant β of neat thiols SAMs was 0.238/CH_2, much smaller than 1.0/CH_2 from literatures, which might be due to the influence of collapsed sites in SAMs or hydrophobic gap on SAMs on the charge transfer resistance of $Fe(CN)_6^{3-/4-}$.

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