

Determination of Surface pKa of Pure Mercaptoacetic Acid and 2-Mercaptobenzothiazole Mixed Monolayers by Impedance Titration

Guang Han LU^{1*}, Chuan Yin LIU^{1,2}, Hong Yan ZHAO¹,
Wei LIU¹, Li Ping JIANG¹, Ling Yan JIANG¹

¹College of chemistry, Central China Normal University, Wuhan 430079

²Department of Chemistry, Yunyang Teacher's College, Danjiangkou Hubei 442700

Abstract: Interfacial proton transfer reactions of pure mercaptoacetic acid (MA) and 2-mercaptobenzothiazole (Mbz) mixed self-assembled monolayers (SAMs) have been studied using a.c. impedance titration method. The charge-transfer resistance (R_{ct}) is measured with the monolayer composition and the ionic strength of pH solution. The surface pKa can be obtained by the plots of R_{ct} and pH, the reasons of shifts of surface pKa are also explained.

Keywords: A.c.impedance titration, mercaptoacetic acid, 2-mercaptobenzothiazole, self-assembled monolayers, surface pKa.

A.c.impedance is applied to monitor the dissociation properties of acidic group on self-assembled monolayers (SAMs) and the effect of supporting electrolyte's pH on surface pKa. There are some reports about determination of the surface pKa using other methods¹. However there are no reports about determination of surface pKa of mercaptoacetic acid SAMs using impedance titration. In this paper, the short-chain molecule mercaptoacetic acid (MA) and 2-mercaptobenzothiazole (Mbz) are used to compose pure and mixed monolayers. The effects of composition of SAMs and ionic strength on the surface acidic dissociation properties of SAMs have been studied and the results of the experiments have also been explained.

Experimental

The gold disk electrode($\Phi=2$ mm) was treated as other papers reported² and immersed in 0.01 mol/L MA or MA+Mbz ethanol solution for 60 h before use.

The cyclic voltammetry was performed using a three-electrode system with SAMs gold electrode as working electrode and saturated calomel electrode (SCE) as the reference electrode. A.c.impedance was performed at the formal potential ($0.13\pm 0.01V$) of the redox probe, which was measured from 10^5 to 0.05Hz at a CHI604 electrochemical analyzer (configuring a.c.impedance analysis software). The supporting electrolyte was

* E-mail: ghlu@ccnu.edu.cn

0.1 mol/L and 0.29 mol/L LiClO₄ + 0.01 mol/L H₃PO₄, using 0.11 mol/L NaOH to adjust the pH to a proper value and required ionic strength.

Results and Discussion

Fe(CN)₆³⁻ was used as an electrochemically active probe molecule to investigate the charge-transfer resistance at bare and pure MA SAMs gold electrode under various experimental conditions. The CVs of the electrochemical behaviors of Fe(CN)₆³⁻ exhibited electrochemically reversible features regardless of the solution pH value at bare gold electrode. As expected from the CVs results, the charge-transfer resistances of probe molecule did not vary with changing solution pH which indicated that Fe(CN)₆³⁻ could arrive at the surface of electrode easily by diffusion-controlled and there was no substance to block off charge-transfer. **Figure 1** shows the complex cyclic voltammograms of MA SAMs in 0.1 mol/L LiClO₄ containing 0.5 mmol/L Fe(CN)₆³⁻. With increase of pH value, the redox peak current decreased and ΔE_p increased. It indicated that the repulsive force increased with increase of pH, indicating that the carboxylic acid group was gradually deprotonated as the pH increased. Consequently, suppressed and irreversible voltammetric behaviors appeared, such as a decrease of peak current and increase of peak splitting. **Figure 2** shows the complex Nyquist plane plots of MA SAMs in 0.1 mol/L LiClO₄ solution containing 0.5 mmol/L Fe(CN)₆³⁻ (ionic strength: 0.1). It can be seen from the plots that the semi-circle diameters in high frequency increased with increase of pH, indicating that the dramatic changes of the R_{ct} were pH dependent. However, in low frequency, Warburg impedance was still a straight line of 45° angle and decreased with increase of pH, which indicated that all the process controlled by diffusion transformed gradually into dynamics controlled³.

The titration curves of impedance for pure and mixed MA SAMs were plotted as a function of solution pH, as shown in **Figure 3**. The pK_{1/2} is defined as the pH value when half of the acid is ionized and can be estimated from the midpoints of inflection of the titration curves. The pK_{1/2} determined for pure MA was 5.20, however pK_{1/2} was 5.30 for mixed SAMs (MA:Mbz=9:1) and 5.60 (MA:Mbz=5:5). The surface pK_{1/2} shifted about 0.5 pH units positively compared with ca. 4.7 for bulk alkanolic acid in 0.1 mol/L LiClO₄. Such positive shifts for pure MA SAMs are consistent with the results obtained from other methods⁴. With adding Mbz, the pK_{1/2} shifted positively might be attributed to a higher dielectric constant and lower molecules' interaction at the MA SAMs.

While the pK_a of carboxylic acid in the bulk solutions is not sensitive to changes in ionic strength, the pK_a of surface-adsorbed acid is highly dependent upon that changes. **Figure 4** shows the complex plots and the impedance titration curves of pure MA and (MA+Mbz) mixed SAMs in 0.4 ionic strength. It can be seen from **Figure 4a** that faster electron transfer kinetics of Fe(CN)₆³⁻ was observed, compared to those in low ionic strength, the reduced R_{ct} indicated that the increase of counterion concentration contributed to the elimination of not only the in-plane interaction at the SAMs but also the repulsion between Fe(CN)₆³⁻ and the carboxylate anions. From **Figure 4b** the pK_a for pure MA was 4.87 and 5.05 for MA+Mbz (5:5), the pK_a shifted negatively for 0.33 and

Figure 1 Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-}$ MA at MA/Au SAMs at different pH

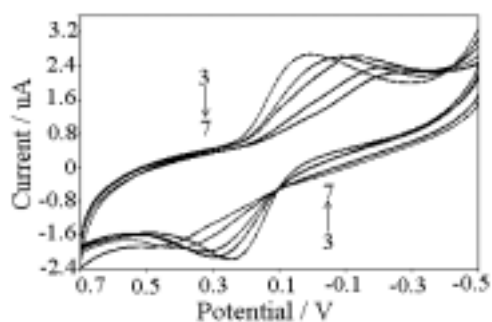


Figure 2 The complex Nyquist plots of SAMs at different pH value(3-7).

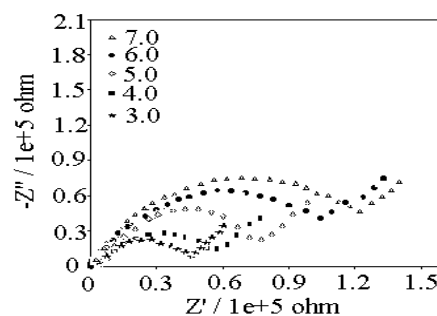


Figure 3 Impedance titration curves for a, b and c

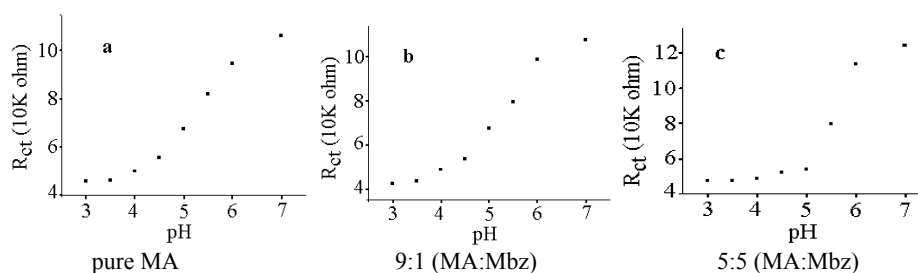
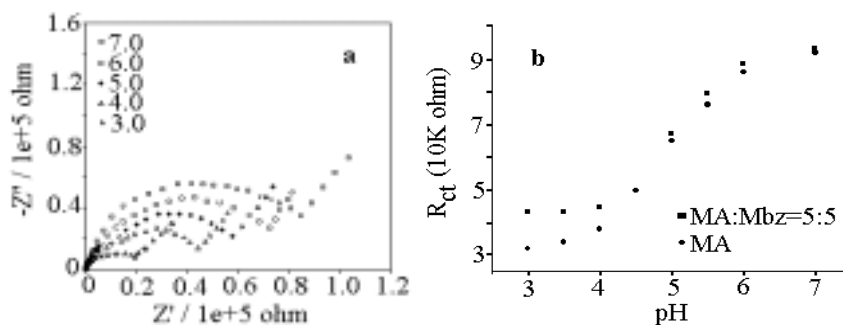


Figure 4 The complex impedance plots of pure MA ($I=0.4$) with different pH (a) and the impedance titration curves ($I=0.4$) (b).



0.55 pH units than in electrolytes whose ionic strength was 0.1 respectively. The results can be explained that the additional interactions and the hydrophobicity of the microenvironments caused by monolayer formations have been perfectly eliminated by the counterions and were accordance with other reports⁶. At a higher ionic strength, the strong hydrogen bonding are blocked due to the formation of ion pairs between $-\text{COO}^-$ and counterions, and adjacent neutral acids can be more easily deprotonated even at low pH value, so the acid group can be dissociate at lower pH and pKa shifts negatively. While at a low ionic strength, the hydrogen bonding would make it to be difficult to dissociate the acids, the pKa shifts to a higher value⁵.

References

1. V. Moliner, E. J. Calvo, *J. Electroanal. Chem.*, **1998**, *445*, 17.
2. H. Y. Chen, D. M. Zhou, J. J. Xu, *et al.*, *J. Electroanal. Chem.*, **1997**, *422*(1-2), 21.
3. S. E. Creager, J. Clarke, *Langmuir*, **1994**, *10*, 3675.
4. J. Zhao, L. Luo, E. Wang, *et al.*, *Electroanalysis*, **1999**, *11*, 1108.
5. K. Kim, J. Kwak, *J. Electroanal. Chem.*, **2001**, *512*, 83.
6. T. Kakiuchi, T. Iida, S. Imabayashi, *et al.*, *Langmuir*, **2000**, *16*, 5397.

Received 23 June, 2003