

Effect of chain length on the surface properties of ω -carboxy alkanethiol self-assembled monolayers

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Self-assembled monolayers (SAMs) of thioglycolic acid, 3-mercaptopropionic acid, 11-mercaptoundecanoic acid, 16-mercaptohexadecanoic acid and bis(carboxydecyl) disulfide are formed on gold electrodes, respectively. The surface pK_a s of the ω -terminal acid groups in these monolayers are determined using electrochemical titration, to be 6.1, 5.3, 7.3, 7.9 and 7.3, respectively. The effect of chain length on the surface pK_a values of ω -carboxy alkanethiol SAMs is described. The SAM has a strong influence on the heterogeneous electron transfer rate constant, k_s , of the electroactive probe $Fe(CN)_6^{3-}$. The k_s values of $Fe(CN)_6^{3-}$, determined with cyclic voltammetry at the pH values of the inflection point of the electrochemical titration curves for the four monolayers with carbon number 2, 3, 11 and 16, are calculated to be 7.4×10^{-3} , 4.6×10^{-3} , 4.4×10^{-3} and $2.6 \times 10^{-3} \text{ cm s}^{-1}$, respectively. The effect of time of immersion for monolayer formation on the defects present in the SAMs formed is discussed. The SAMs of bis(carboxydecyl) disulfide and 11-mercaptoundecanoic acid show the same surface pK_a and k_s values and thus possess the same surface properties.

Introduction

Self-assembled monolayers, especially those of ω -functionalized alkanethiols on gold, have received considerable attention because they provide a means to control interfacial properties for different applications. The interfacial specific interactions of SAMs have been evaluated by many techniques such as corrosion prevention,^{1,2} wear protection,^{3,4} molecular recognition,⁵⁻⁷ electrochemical determination,^{8,9} electrochemical^{10,11} and biosensors.^{12,13} The formation of ω -substituted alkanethiol monolayers is a powerful and convenient method for creating surfaces with specific functional groups. For example, the further derivation of the ω -carboxy or ω -amino substituted thiols has been used for immobilizing proteins,¹⁴ polypeptides,¹⁵ DNA,¹⁶ polyelectrolytes¹⁷ and metal ion by controlling the electric state of the monolayer.¹⁸ The design of a surface with a SAM is based on the properties of the immobilized molecules, thus precise control of the surface function and surface properties become very important as the assembly technique is improved. Surface pK_a is one of the most important parameters of the surface properties. It shows not only the acidity and interfacial proton transfer reaction of the SAM terminal group, but also the electric state of the SAM surface. Thus its determination and control are of significance in both practice and theory. Many techniques have been developed to determine surface pK_a values of ω -carboxy alkanethiol self-assembled monolayers, such as contact angle titration,^{19,20} chemical force titration using atomic force microscopy (AFM),^{21,22} the quartz crystal microbalance (QCM),^{23,24} surface potential,²⁵ spectroscopy,²⁶ a laser-induced temperature jump technique (ILIT)²⁷ and an electrochemical method.²⁸ The effect of chain length on the surface pK_a of ω -mercaptoalkanoic acid SAMs has been considered by Kakiuchi *et al.*²⁹ and Shimazu *et al.*²⁴ and the mixed monolayers of ω -mercaptoalkanoic acid with alkanethiols of vari-

able chain length have also been studied with the contact-angle titration method^{20,30} and voltammetry,³¹ however, there has been little discussion about the relationship between the chain length of the ω -mercaptoalkanoic acid on gold and the surface pK_a .

The different methods that have been used to determine the surface pK_a of ω -carboxyl alkanethiol SAMs give different results. For example, the surface pK_a of 11-mercaptoundecanoic acid was found to be 10.3 by double-layer-capacitance,²⁹ 6.1 ± 0.1 by QCM,²⁴ 5.7 ± 0.2 by ILIT²⁷ and 3.0 ± 0.2 by electrochemical titration.³² The surface pK_a of 3-mercaptohexanoic acid was found to be 7.7 by double-layer-force measurement,³³ 6.0 by QCM,²⁴ 5.6 by contact angle titration and 5.2 by electrochemical titration.³⁴ In order to study the effect of chain length on the surface pK_a , the surface pK_a values of ω -mercaptoalkanoic acid with extensively variable chain length should be measured accurately with a sensitive and simple method. The double-layer-capacitance titration is applicable only for SAMs with a shorter chain length,²⁹ and the surface pK_a values obtained are much larger than those obtained by other methods when the carbon number is more than 10. On the other hand, the determination of surface pK_a by using QCM, AFM and ILIT is comparatively inconvenient. The QCM technique gave a very small shift in surface pK_a when the carbon number increased from 10 to 16.²⁴ The shift is less than that in solution. Electrochemical titration has proved to be a sensitive and convenient technique.³⁴ This technique can measure both the acidity of the monolayers and the state of the adsorbed monolayer on the electrodes.

Here we use electrochemical titration to determine the surface pK_a of ω -mercaptoalkanoic acid with variable chain length, with carbon numbers from 2 to 16. When the carbon number is 2, a higher surface pK_a value than that for a carbon number of 3 is observed. A detailed interpretation of the effect of the chain length of ω -mercaptoalkanoic acid on the surface