CHEMCOMM
Communication
www.rsc.org/chemcomm

Detection of difference in acidity between arrayed carboxy groups and the groups dissolved in solution by reductive desorption of a self-assembled monolayer of carboxy-terminated thiols†

Hirokazu Munakata and Susumu Kuwabata*

Department of Materials Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan. E-mail: kuwabata@chem.eng.osaka-u.ac.jp

Received (in Cambridge, UK) 2nd March 2001, Accepted 6th June 2001
First published as an Advance Article on the web 4th July 2001

The pK_a value of arrayed carboxy groups and that of groups dissolved in solution can easily be determined by electrochemical desorption of a self-assembled monolayer of carboxy-terminated thiols in aqueous solutions.

Monolayers composed of closely packed organic species are of great interest as models of biomembranes. In particular, monolayers containing acidic and basic groups are useful for understanding roles of those species in various functions of cell membranes, such as cell fusion, enzymatic catalysis, and ion transfers. One of the well-known specific properties of closely arrayed groups is that acidities of groups like carboxy and amino are different from their original values. Such behaviour has been first found by potentiometric titration of micellar solutions of various surfactants.[1] A self-assembled monolayer (SAM) of alkanethiols adsorbed on a gold surface provides another monolayer system. Ease of preparation of the organized monolayer with high reproducibility and high stability of the resulting monolayer facilitate investigation of the properties of monolayers.[2] If alkanethiols substituted by functional groups at ω-positions are used, one can prepare a surface in which the functional groups are closely arrayed. In this case also, determination of acidity of the arrayed groups is currently attracting great attention. To detect properties of the delicate monolayer surfaces special techniques must be adopted, paying deliberate attention to such matters as measurements of contact angles of water drops on the thiol-SAM,[3] the double layer interaction measurements using the atomic force microscope,[4] double layer capacitance measurements by AC impedance spectroscopy,[5] and quartz crystal microbalance measurements.[6] In some cases, the help of difficult theory and calculations is needed to determine the desired parameters. We would like to show herein that electrochemical desorption reaction of a thiol-SAM measured by conventional voltammetry becomes a useful method to evaluate acidity, *i.e.* pK_a, of the groups substituted to the terminals of alkanethiols. This method allows direct determination of not only pK_a value of the arrayed groups but also that of the groups dissolved in solution simultaneously from the obtained titration curve. In this paper, a typical method is introduced by showing the results obtained for a SAM of 3-mercaptopropionic acid (MPA) formed on a gold substrate.

The gold substrate used in this study was an Au-coated mica having a quasi (111) surface [Au(111)], which was prepared by vacuum evaporation of Au.[7] The mica sheet was heated at 300 °C for at least 2 h prior to evaporation and heating was maintained during deposition and post-annealing for 1 h. Formation of a MPA-SAM on the Au(111) electrode was conducted by immersion of the electrode in an ethanolic solution containing 1 mmol dm^{-3} MPA for 1 h. The resulting electrode is denoted here as MPA/Au(111). Reductive desorption experiments were carried out in 0.1 mol dm^{-3} phosphate buffer solutions prepared by using Milli-Q gradient A10 water (ρ > 18.2 MΩ cm). The electrolysis cell was a one-compartment cell having Ag/AgCl in KCl-saturated aqueous solution and a Pt foil electrode as reference and counter electrodes, respectively. The MPA/Au(111) electrode was placed at the bottom hole of the cell with a Teflon-coated O-ring, giving an effective surface area of 0.4 cm^2.[7]

Fig. 1 shows linear sweep voltammograms of the MPA/Au (111) electrodes taken at 200 mV s^{-1} in buffer solutions having pH 3.57, 5.98, 7.04, 8.04, 8.85, and 9.97. The cathodic waves representing reductive desorption of MPA-SAM appeared and their peak potentials were negatively shifted with increasing pH of the electrolyte solution. In general, the reductive desorption of an alkanethiol-SAM was made by using highly alkaline solutions.[8] In those cases, the reaction can be formulated as Au–S–R + e$^-$ → Au + $^-$S–R where R denotes an alkyl group. However, since pH values of the solutions chosen in this study were smaller than pK_a of thiol group in MPA, which is 11,[9] the group must be protonated when MPA is dissolved in the solutions. As a result, the desorption reaction can be given by eqn. (1).

$$\text{Au–S–R} + e^- + H^+ \rightarrow \text{Au} + \text{HS–R} \tag{1}$$

This equation including one proton and one electron predicts negative shifts of the reaction potential with an increase in pH of the electrolyte solution. The integration of each current peak shown in Fig. 1 gave a charge density of 71 (± 4) × 10^{-6} C cm^{-2}, allowing an estimate of the amount of adsorbed MPA to be 0.74 (± 4) × 10^{-9} mol cm^{-2}. The obtained values were close to the coverage (0.77 × 10^{-9} mol cm^{-2}) expected for a ($\sqrt{3} \times \sqrt{3}$)R30° overlayer structure of alkanethiols on a Au(111) surface.[8]

Plots of cathodic peak potentials as a function of pH of the electrolyte solution gave the relationship shown in Fig. 2. Since the obtained graph has two distinct bending points at pH = 4.3 and 7.5, the pH regions of pH < 4.3, 4.3 < pH < 7.5, and 7.5

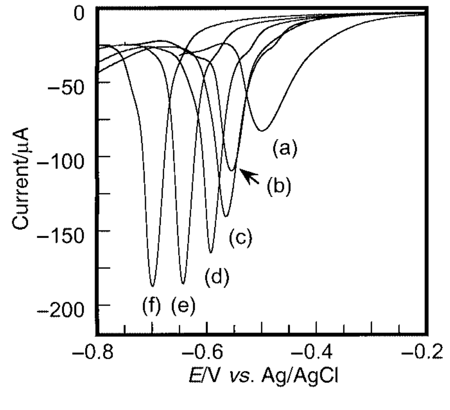

Fig. 1 Linear sweep voltammograms of MPA/Au(111) electrodes taken at 200 mV s^{-1} in 0.1 mol dm^{-3} phosphate buffer having pH of (a) 3.57, (b) 5.98, (c) 7.04, (d) 8.04, (e) 8.85, and (f) 9.97.

---

† Electronic supplementary information (ESI) available: titration curves from linear sweep voltammograms. See http://www.rsc.org/suppdata/cc/b1/b102601c/

DOI: 10.1039/b102601c

This journal is © The Royal Society of Chemistry 2001

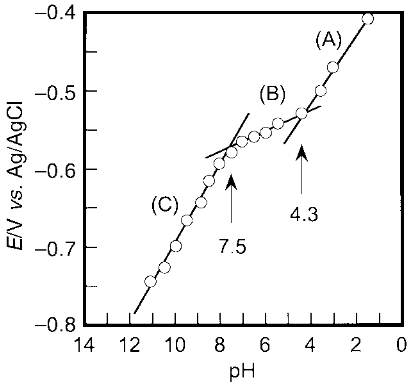

Fig. 2 Plots of peak potentials of cathodic waves due to reductive desorption of MPA as a function of pH of the electrolyte solution.

$<$ pH are denoted here as the regions (A), (B), and (C), respectively. At the regions (A) and (C), linear relations were observed and the same slope of -50 mV per pH unit was estimated. If the eqn. (1) occurs, the experimentally obtained slope was a little smaller than the value (-59 mV per pH unit) expected from the Nernst equation. In the case of the reductive desorption of the thiol-SAM, protons in the electrolyte solution need to penetrate through the closely packed alkyl chains of the thiols in the initial stage. It is then suggested that some time is required for the pH around the sulfate groups to become the same as that of the solution bulk. Such kinetic factors seem to be the cause of differences between the experimentally obtained slope and the theoretical one.

The finding that one of the bending points appeared at pH = 4.3 coincident with the pK_a value of carboxy group of MPA,[9] allowed us to regard R in eqn. (1) as $(CH_2)_2$–COOH and $(CH_2)_2$–COO^- at the regions (A) and (C), respectively. However, a small pH dependence of -10 mV per pH unit was observed at the region (B). As mentioned in the introductory remarks, closely arrayed carboxy groups possess pK_a values that differ from the original. In the case of the MPA-SAM on Au(111) electrode, values ranging from 5.8 to 8 were evaluated by atomic force microscopy,[4] AC impedance,[5] and quartz crystal microbalance measurements.[6] If such a phenomenon is considered, one can imagine that there is a pH region where carboxylic acid groups in MPA-SAM are protonated but deprotonated in the solution. By combining this idea with the reductive desorption reaction given by eqn. (1), the reaction given in eqn. (2) is appropriate at that pH region.

$$\text{Au–S–(CH}_2)_2\text{–COOH} + e^- \rightarrow \text{Au} + \text{HS–(CH}_2)_2\text{–COO}^- \quad (2)$$

The deprotonation of the carboxy group and protonation of the generated thiolate take place simultaneously, resulting in the exclusion of protons from the reaction. The reaction having lower pH dependence observed at the region (B) is attributable to the reaction given by eqn. (2) and pH = 7.5 where another bending point appeared can be regarded as the pK_a value of the carboxy groups in MPA-SAM. Nevertheless a pH dependence of -10 mV per pH unit was observed at this region, but this might be also due to the kinetic factors mentioned above.

The desorption experiments were made at 10, 50, and 200 mV s^{-1}. The peak potential was positively shifted with a decrease in the sweep rate because of abatement of potential drop in the monolayer, as already shown in our previous paper.[10] Interestingly, however, the titration curves obtained from the voltammograms taken at different sweep rates (see Fig. S1) exhibited bending points at the same pH within experimental errors of ± 0.1, indicating that the above-mentioned kinetic factors did not affect pK_a values estimated by this method. The investigations aiming to elucidate the kinetic factors and applicability of the method developed in this study are underway.

We thank Dr Araki Masuyama for stimulating discussions. This research was supported by CREST of JST (Japan Science and Technology Corporation) and by the Millennium Project (No. 12310) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Notes and references

1 F. Van Voorst Vader, *Trans. Faraday Soc.*, 1961, **57**, 2263; F. Van Voorst Vader, *Trans. Faraday Soc.*, 1963, **59**, 1225; F. Tokiwa and K. Ohki, *J. Phys. Chem.*, 1967, **71**, 1824.

2 For review, see A. Ulman, *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*, Academic Press, Boston, 1991; H. O. Finklea, in *Electroanalytical Chemistry*, ed. A. J. Bard and I. Rubinstein, Marcel Dekker, New York, 1996, vol. 19, p. 109; A. Ulman, *Chem. Rev.*, 1996, **96**, 1533.

3 S. R. Holmes-Farley, R. H. Reamey, T. J. McCarthy, J. Deutch and G. M. Whitesides, *Langmuir*, 1985, **1**, 725; C. D. Bain and G. M. Whitesides, *Langmuir*, 1989, **5**, 1370; T. R. Lee, R. I. Carey, H. A. Biebuyck and G. M. Whitesides, *Langmuir*, 1994, **10**, 741; R. C. Chatelier, C. J. Drummond, D. Y. C. Chan, Z. R. Vasic, T. R. Gengenbach and H. J. Griesser, *Langmuir*, 1995, **11**, 4122.

4 K. Hu and A. J. Bard, *Langmuir*, 1997, **13**, 5114.

5 M. A. Bryant and R. M. Crooks, *Langmuir*, 1993, **9**, 385; K. Aoki and T. Kakiuchi, *J. Electroanal. Chem.*, 1999, **478**, 101; T. Kakiuchi, M. Iida, S. Imabayashi and K. Niki, *Langmuir*, 2000, **16**, 5397.

6 J. Wang, L. M. Frostman and M. D. Ward, *J. Phys. Chem.*, 1992, **96**, 5224; K. Shimazu, T. Teranishi, K. Sugihara and K. Uosaki, *Chem. Lett.*, 1998, 669; K. Sugihara, T. Teranishi, K. Shimazu and K. Uosaki, *Electrochemistry*, 1999, **67**, 1172; K. Sugihara, K. Shimazu and K. Uosaki, *Langmuir*, 2000, **16**, 7101.

7 D. Oyamatsu, M. Nishizawa, S. Kuwabata and H. Yoneyama, *Langmuir*, 1998, **14**, 3298; D. Oyamatsu, S. Kuwabata and H. Yoneyama, *J. Electroanal. Chem.*, 1999, **473**, 59.

8 C. A. Widrig, C. Chung and M. D. Porter, *J. Electroanal. Chem.*, 1991, **310**, 335; M. M. Walczak, D. D. Popenoe, R. S. Deinhammer, B. D. Lamp, C. Chung and M. D. Porter, *Langmuir*, 1991, **7**, 2687; S. Imabayashi, M. Iida, D. Hobara, Z. Q. Feng, K. Niki and T. Kakiuchi, *J. Electroanal. Chem.*, 1997, **428**, 33; S. Imabayashi, N. Gon, T. Sasaki, D. Hobara and T. Kakiuchi, *Langmuir*, 1998, **14**, 2348.

9 W. P. Jencks and J. Regenstein, in *Handbook of Biochemistry and Molecular Biology*, ed. G. D. Fasman, CRC Press, Cleveland, 1976, vol. 3, p. 305.

10 H. Munakata, S. Kuwabata, Y. Ohko and H. Yoneyama, *J. Electroanal. Chem.*, 2001, **496**, 29.