ELECTROCHEMICAL PROPERTIES OF ADSORBED ALKANETHIOL MONOLAYERS ON MERCURY ELECTRODE SURFACES

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Abstract *n*-Alkanethiols ($\text{CH}_3(\text{CH}_2)_n\text{SH}$, $n=3,5,11,13,15,17$) have been adsorbed at mercury electrodes from ethanolic solutions. A. c. voltammetry has been carried out of the adsorbed alkanethiol on mercury electrodes in aqueous solutions containing 1 M KCl at 25°C. Cyclic d.c. voltammetry of several metal ions also has been performed at these electrodes. The results show that long-chain alkanethiols $n \geq 11$ can form densely packed monolayers with fully extended alkyl chains in the potential range between 0 and -0.7 volt vs. Ag/AgCl. Metal ions such as Pb^{2+} are unable to penetrate into the monolayer. In contrast, short-chain alkanethiols with $n = 3$ and 5 form less ordered and loosely packed adsorption layers, which are permeable to the metal ions. A pH dependent a.c. voltammetric peak is observed at a mercury electrode with adsorbed alkanethiol ($n=5$) in buffer solutions, which is attributable to the redox reaction of the adsorbed thiol: $[\text{CH}_3(\text{CH}_2)_5\text{S}]_{\text{ad}}\text{Hg} + \text{H}^+ + \text{e}^- \rightleftharpoons [\text{CH}_3(\text{CH}_2)_5\text{SH}]_{\text{ad}}\text{Hg}$.

Key words alkanethiol, mercury electrode, differential capacitance

Organosulfur compounds can form monolayer films on a variety of metal substrates[1]. The formation of these films proceeds spontaneously by immersing the substrates into the solution containing the organosulfur compounds, which provide a convenient technique for the preparation of compact monolayers with controlled thickness and structure[2]. Among these monolayers, those formed at Au from *n*-alkanethiols and their substitute analogs have been extensively studied[2,3]. Very recently, monolayer films of *n*-alkanethiols at Ag have also been studied[1]. The films at Ag are more densely packed and more resistant to ion transport in comparison with the films at Au, pointing to a difference in the bonding between the head group and the metal. For the factors in determining such a structure of the monolayers on different substrates, the crystallinity and the electronic properties of the metal substrates are considered[1]. In this respect, we have interested in Hg. Mercury is in a liquid state and shows high affinity to sulfur, therefore it may be a suitable substrate to form a compact uniform monolayer which is free from defects. A mercury electrode has advantages that a fresh electrode surface can be easily obtained with good reproducibility and it is smooth and free from the problem of surface roughness which is often troublesome in the case of solid electrodes[4]. This paper reports our results of electrochemical studies of adsorbed *n*-alkanethiols on mercury electrodes.

EXPERIMENTAL

Reagents *n*-Alkanethiols ($\text{CH}_3(\text{CH}_2)_n\text{SH}$, $n=3,5,11,13,15,17$) were obtained from Tokyo Kasei Kogyo Co. Ltd., and were used as received. All other reagents used were of analytical-reagent grade.

Apparatus Cyclic voltammetry was performed with a Fuso 311 potentiostat in conjunction with a Fuso 1104 multi-sweep unit. A. c. voltammetry was carried out with the above mentioned potentiostat, d.c. voltage sweeper, an NF LI-574 lock-in amplifier and an Iwatsu FG-330 a.c. voltage generator. The resistive (in-phase) and capacitive (out-of-phase) components of the a.c. voltammograms were recorded. All voltammograms were recorded with Watanabe WX4302 X-Y recorder.

Adsorption of *n*-alkanethiols on a mercury electrode A Metrohm E410 hanging

mercury drop electrode (HMDE) was used. The HMDE was immersed in an ethanolic solution containing *n*-alkanethiol in a concentration (c_n) 0.1 or 0.5 mM and a fresh mercury drop was produced, the surface area of which was $0.0187 \pm 0.0003 \text{ cm}^2$. The electrode was kept in the solution for a given period of time (t_{exp}), during which time *n*-alkanethiol was allowed to adsorb on the electrode surface, then the electrode was removed and rinsed with absolute ethanol first and then deionized-water. The HMDE with the adsorbed *n*-alkanethiol was immediately immersed in a aqueous solution and electrochemical measurements were done.

Electrochemical measurements All electrochemical measurements were carried out at $25 \pm 0.1^\circ \text{C}$ with a three electrode system in an deaerated aqueous solution containing 1M KCl, unless stated otherwise. To prepare the solution, deionized water from a Nanopure II purification system (Barnstead Co.) was used. In a.c. measurements the amplitude of the superimposed a.c. voltage was adjusted to 2 mV (effective value) and the frequency to 50 Hz. Potentials were measured against an Ag/AgCl (saturated KCl) electrode.

RESULTS AND DISCUSSION

Fig. 1 Imaginary component of a.c. voltammograms recorded in 1M KCl solution. A) bare HMDE, B) and C) HMDE with alkanethiol($n=11$) adsorbed for $t_{\text{exp}}=1\text{min}$ from the ethanolic solutions of c_n = B) 0.5 mM and C) 0.1 mM. D.c. voltage scan was started from 0 V at the scan rate 2mV/s.

A.c. voltammetric measurements for different electrodes with adsorbed alkanethiol($n=11$) gave nearly the same a.c. voltammograms. At some potential below -0.65V current steeply increased (Fig. 1B and 1C). This abrupt rise of current appears centered at -0.7V in the range of 100mV for $c_n = 0.5\text{ mM}$ and at about -0.79V for $c_n = 0.1\text{ mM}$ in several experiments.

The results indicate that the structure of the adsorbed alkanethiol($n=11$) on Hg depends on its concentration in ethanolic solutions from which it is adsorbed. The potential-independent small current between 0 and -0.7V in Fig. 1B indicates it forms a compact adsorption layer on Hg in this potential range when adsorbed from 0.5 mM solution. Differential capacitance peaks observed in Fig. 1C suggest that its structure on Hg changes with potential when adsorbed from 0.1 mM solution, which means the structure is less compact. Steep current rise at a potential below -0.7V in both cases of

Fig. 1A shows dependence of the imaginary component of the a.c. current (I_{im}) at a bare HMDE in 1M KCl solution on the potential applied to the electrode. The corresponding real component was negligibly small in magnitude. The differential capacitance (C_d) was calculated from this figure to be $35.4 \mu\text{F/cm}^2$ at -0.472V (the potential of zero charge of bare Hg-1M KCl solution interface: E_{pzc}) which agreed well with the reported value $39.0 \mu\text{F/cm}^2$ [5]. As shown in Fig. 1B and 1C, I_{im} drastically decreased when alkanethiol($n=11$) was adsorbed on an HMDE. Two large peaks were observed at -0.14 V and -0.70 V (Fig. 1C) when adsorbed from the solution of $c_n = 0.1\text{ mM}$ for $t_{\text{exp}} = 1\text{ min}$. Practically the same voltammograms were obtained for longer exposure times $t_{\text{exp}} = 5, 10$ and 20 min . On the other hand, an HMDE with alkanethiol($n=11$) adsorbed from a solution of $c_n = 0.5\text{ mM}$ for $t_{\text{exp}} = 1\text{ min}$ produced no a.c. voltammetric peaks (Fig. 1B); I_{im} was independent of the potential applied to the electrode between 0 and -0.80V , and was smaller in magnitude than that in Fig. 1C in this potential range. The same voltammogram was obtained with the electrode for $t_{\text{exp}} = 10\text{ min}$.

$c_n = 0.5$ and 0.1 mM indicates a drastic change of the adsorption layer at such negative potentials.

A.c. voltammograms of adsorbed alkanethiols ($n=13, 15$ and 17) on Hg were recorded similarly. When they were adsorbed from both $c_n = 0.1$ and 0.5 mM solutions, voltammograms similar in shape to that in Fig. 1C and that in Fig. 1B were obtained for $n = 13$ and for $n = 15$ and 17 , respectively.

Differential capacitances were calculated from I_{im} at -0.472 V and are given in TABLE 1, in which the numerical values are the average of the measurements on different electrodes of the number given in parentheses.

TABLE 1 Differential capacitance of the mercury electrodes with adsorbed alkanethiol in 1 M KCl solution at -0.472 V vs. Ag/AgCl (25°C)

n	$C_d / \mu\text{F cm}^{-2}$		
	$c_n = 0.1$ mM	0.5 mM	Au ^{a)}
3	25.6	$25.3 \pm 1.54(3)$	40
5	$17.2 \pm 0.45(2)$	$19.5 \pm 0.85(2)$	18
11	$1.59 \pm 0.158(5)$	$1.13 \pm 0.068(7)$	$1.42(1.52)$
13	1.44	$1.12 \pm 0.105(2)$	—
15	$1.17 \pm 0.052(4)$	$1.07 \pm 0.020(2)$	1.09
17	0.797	0.731	$0.948(1.00)$

a) The values for gold electrodes, which were read from the plot of reciprocal of capacitance against n in Fig. 7 of ref. [3]. The values were obtained at $+0.3$ V from the linear sweep voltammetry at 100mV/s (10 mV/s in parentheses).

Fig. 2 Cyclic voltammograms of Pb^{2+} , Cd^{2+} and Zn^{2+} (0.2 mM each) in a solution containing 0.5 M ammonium acetate and 0.1 M tartaric acid. A) bare Hg electrode, B) and C) Hg electrodes with adsorbed alkanethiols of $n=5$ and $n=15$, respectively. $c_n=0.5$ mM, $t_{\text{exp}}=10$ min. Scan rate: 200mV/s .

A bare Hg electrode gives well defined redox waves with the cathodic peaks at -0.44 , -0.59 and -1.07 V for Pb^{2+} , Cd^{2+} and Zn^{2+} , respectively (Fig. 2A). On the other hand, the Hg electrode with adsorbed alkanethiol ($n=15$) (Fig. 2C) gives no wave for the reduction of Pb^{2+} at the corresponding potential.

This table also includes the data for $n = 3$ and 5 obtained similarly. The a.c. voltammograms of these adsorbed thiols were comparable both in shape and magnitude to those of bare Hg. These results indicate that short-chain alkanethiols with $n = 3$ and 5 form loosely packed adsorption layers on Hg. Differential capacitances for longer chains $n \geq 11$ are much smaller. When $c_n = 0.5$ mM, they are smaller than those for alkanethiol monolayers on gold electrodes (column 4 in table 1). Since the long-chain alkanethiols are known to form a densely packed monolayer with fully extended alkyl chains tilted from the Au surface normal by $\sim 30^\circ$ [3], we may conclude that they also form a packed monolayer on Hg surface with the alkyl chains being fully extended but probably less tilted than the case of Au. Recently, it is reported that the alkyl chains of the adsorbed long-chain alkanethiol monolayers at Ag are tilted only $\sim 13^\circ$ from the surface normal [4]. This is also consistent with our results on Hg.

Fig. 2 shows cyclic voltammograms of metal ions at the mercury electrode with adsorbed alkanethiols.

One large cathodic peak appears at -0.70V and the wave for the reduction of Zn^{2+} follows. The result indicates that the adsorbed alkanethiol($n=15$) film on Hg is so densely packed that Pb^{2+} ion is unable to penetrate into the film to react with the metal substrate directly, and both Pb^{2+} and Cd^{2+} ions are reduced simultaneously at the potential lower than the peak potential of Cd^{2+} at a bare Hg electrode. This is consistent with the above results that differential capacitances for Hg electrodes with adsorbed long-chain thiols($n \geq 11$) are small and constant in the range of 0 to -0.7V . In contrast, the Hg electrode with alkanethiol($n=5$) (Fig. 2B) produces redox waves at the peak potentials corresponding to those of the waves at a bare Hg electrode, indicating it forms a loosely packed adsorption film on Hg. This is also consistent with the results of a.c. voltammetry.

Fig.4 Dependence of the peak potential on pH.

Fig. 3 A.c. voltammograms of (A) imaginary and (B) real component recorded in a 10-fold-diluted McIlvaine buffer solution (pH 7.0) containing 1M KCl at the Hg electrode with adsorbed alkanethiol($n=5$), $c_n=0.5 \text{ mM}$, $t_{\text{exp}}=1\text{min}$. D.c. voltage scan was started from 0 V at the scan rate 2mV/s .

Mercury electrodes show high affinity to sulfur compounds, and often produce redox waves due to the redox reaction of thiol compounds[6]. We examined redox waves for the adsorbed alkanethiols in buffer solutions. As shown in Fig. 3, an Hg electrode with adsorbed alkanethiol($n=5$) produced a.c. voltammetric waves in both imaginary and real components at almost the same peak potentials (E_p) (peaks at about -0.495 V in Fig. 3). This peak was pH dependent and E_p shifted by -60 mV per pH (Fig. 4). We may consider that the adsorbed alkanethiol($n=5$) on an Hg electrode show a redox reaction (1).

Further study of the redox reaction is under way in our laboratory. When an Hg electrode with adsorbed alkanethiol($n=11$) was used, no waves ascribable to eq.(1) was observed. Considering the above indication that it forms a compact film on Hg, we can infer that solvent molecules such as hydronium ions may be unable to access to this electrode surface.

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