Electronic Supplementary Information

Probing interfacial solvation of incipient self-assembled monolayers

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1. Experimental details

1.1. Reagents

Ethanethiol, 1-Propanethiol, 1-Butanethiol, 1-Pentanethiol, 1-Hexanethiol, 1-Heptanethiol, 1-Octanethiol, 1-Nonanethiol, 1-Decanethiol, 1-Undecanethiol, 1-Dodecanethiol, 6-Mercatohexanoic acid, 8-Mercaptooctanoic acid, 11-Mercaptoundecanoic acid, 12-Mercaptododecanoic acid, 15-Mercaptopentadecanoic acid and 16-Mercaptohexadecanoic acid were purchased from Aldrich. Sodium hydroxide and ethanol were purchased from Fluka Chemicals and Merck, respectively. All chemicals were used as received. Aqueous solutions were prepared from water purified with a Millipore Milli-Q system (resistivity 18 MΩ cm). Working solutions of 5µM thiol in 0.5M NaOH were prepared from a 5 mM stock solution of thiol in ethanol, so that the concentration of ethanol in the electrochemical cell was 0.015 M. These solutions were prepared daily and deaerated with a presaturated argon stream prior to the measurements. Mercury was distilled three times under vacuum after treatment with dilute nitric acid and mercurous nitrate.

1.2. Deposition of thiols at low surface coverages

Deposition of the studied thiols onto the mercury surface was carried out *in situ*, under potentiostatic control, from solutions containing 5 µM thiol, 0.5 M NaOH and 0.015 M ethanol, so that the deposition rate on each newly grown mercury drop was diffusion limited. Under these conditions, the amount of adsorbed thiol at low surface coverages was modulated by varying the deposition time within the 1 - 5 s range. For each thiol, a set of cathodic stripping voltammograms was recorded for distinct preconcentration times, differing by one second. Then, the voltammogram whose background-corrected cathodic area was closest to 2.4 µC cm^{-2} (=25 pmol cm^{-2}) was chosen and normalized to 25 pmol cm^{-2}. The surface concentrations of the selected voltammograms were always within the 25 ± 3 pmol cm^{-2} interval. For most of the studied thiols a deposition time of 1 or 2 seconds was enough to reach a surface concentration of ~ 25 pmol cm^{-2}, without a clear systematic variation with the alkyl chain length. However, slightly longer deposition times were required for ethanethiol (4 s) and dodecanethiol (5 s). In the former case, the reason

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may be a decrease of the thiol bulk concentration with respect to the nominal one due to its volatilization, whereas in the second case it may result from either a lower solubility or a lower diffusion coefficient of dodecanethiol. In order to keep the same time window between the end of the deposition step and the onset of reductive desorption, depositions were carried out at a potential 0.3V more positive than the peak potential. On the other hand, the use of a low bulk thiol concentration ensures that freely-diffusing thiol molecules do not interfere with the electrochemical signal generated during the stripping step.

1.3. Electrochemical measurements

Electrochemical measurements were carried out in a water-jacketed glass cell, thermostated at 0 ± 0.2ºC with a Haake D8.G circulator thermostat. A Ag/AgCl/NaCl(sat.) electrode and a platinum foil were used as reference and auxiliary electrodes, respectively. The working electrode was a hanging mercury drop electrode (EG&G PAR 303A) whose area (0.0267 cm^2) was determined by weighing three sets of ten drops. Cathodic stripping voltammograms were recorded at 1 V s^{-1} with an Autolab PGSTAT30 (Eco Chemie B. V.).

2. Raw cathodic stripping voltammograms for the studied thiols

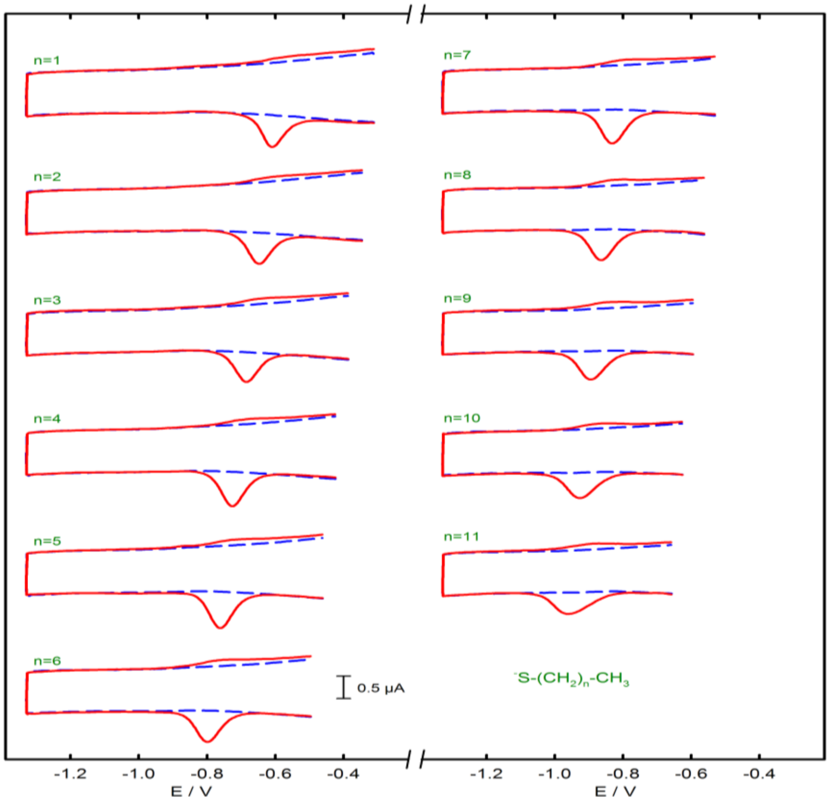

Fig. S1 Raw cathodic stripping voltammograms measured in a solution containing 0.5 M NaOH, 0.015M ethanol (blue lines), or 5 µM the indicated *n*-alkanethiol, 0.5 M NaOH and 0.015 M ethanol (red lines). Deposition potential was 0.3 V with respect to the peak potential. Deposition times were adjusted to keep the surface concentration of thiol at 25 pmol cm^{-2}. Scan rate 1 V s^{-1}. T = 298 K.

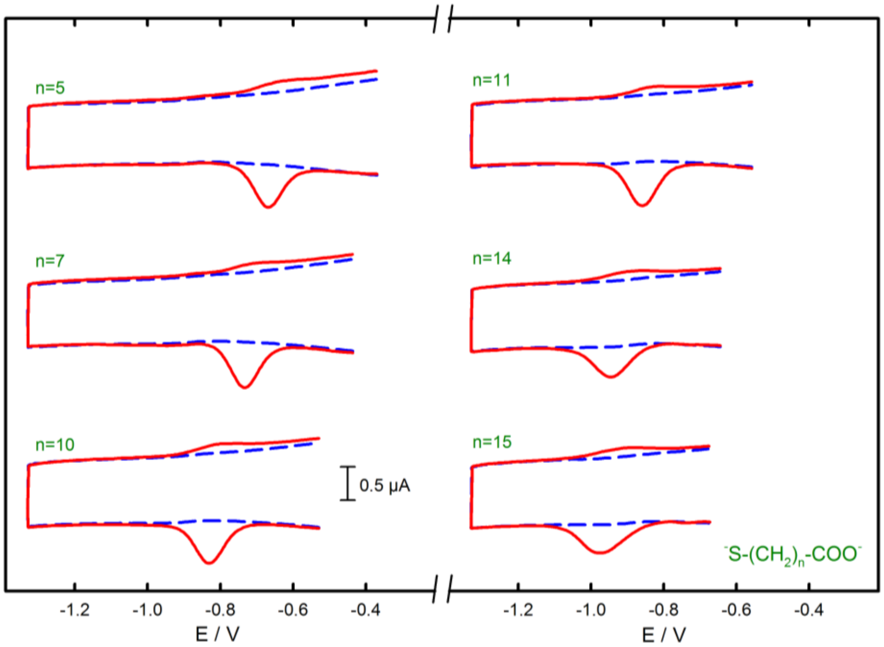

Fig. S2 Raw cathodic stripping voltammograms measured in a solution containing 0.5 M NaOH, 0.015 M ethanol (dashed blue lines), or 5 μM the indicated *n*-carboxyalkylthiol, 0.5 M NaOH and 0.015 M ethanol (solid red lines). Deposition potential was 0.3V with respect to the peak potential. Deposition times were adjusted to keep the surface concentration of thiol at 25 pmol cm^{-2}. Scan rate 1 V s^{-1}. T = 298 K.

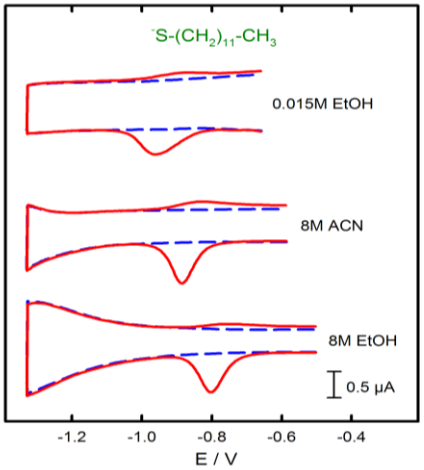

Fig. S3 Raw cathodic stripping voltammograms measured for 1-dodecanethiol deposited on a mercury electrode from solutions containing 5 μM 1-dodecanethiol, 0.5 M NaOH and the indicated concentration of ethanol or acetonitrile. Deposition potential was 0.3 V with respect to the peak potential. Deposition times were adjusted to keep the surface concentration of 1-dodecanethiol at 25 pmol cm^{-2}. Scan rate 1 V s^{-1}. T = 298 K.

3. Theoretical cathodic stripping voltammetric response

The cathodic stripping voltammetric response of a redox couple whose reduced form is freely-diffusing and its oxidized form is strongly adsorbed can be described with the following mechanism:

$$\begin{gathered} R + MS \xrightleftharpoons{K_{a,R}} MR + S \\ MR \xrightleftharpoons{E_s} MO + ne^- \end{gathered} \tag{S.1}$$

where the first step represents the adsorption/desorption of the reduced form, characterized by the equilibrium constant $K_{a,R}$, and the second step represents it surface redox conversion, characterized by the standard formal potential E_S. R and O stand for the reduced and oxidized forms of the redox couple, respectively; and S for the solvent.

The corresponding boundary value problem in spherical coordinates is defined by Fick's second law for the mass transport of the freely-diffusing reactant R:

$$\frac{\partial c_R}{\partial t} = D_R \frac{\partial^2 c_R}{\partial r^2} + \frac{2D_R}{r}\frac{\partial c_R}{\partial r} \tag{S.2}$$

with the following initial and boundary conditions:

$t = 0, r \geq r_o$:

$$c_R(r,0) = c_R^b \tag{S.3}$$

$$\Gamma_R(0) = \frac{K_{a,R} c_R^b \Gamma_R^{\max}}{c_S^b + K_{a,R} c_R^b} \tag{S.4}$$

$$\Gamma_O(0) = 0 \tag{S.5}$$

$t > 0, r = \infty$:

$$c_R(\infty,t) = c_R^b \tag{S.6}$$

$t > 0, r = r_o$:

$$D_R\left(\frac{\partial c_R}{\partial r}\right)_{r=r_o} = \frac{d\Gamma_R}{dt} + \frac{d\Gamma_O}{dt} \tag{S.7}$$

$$K_{a,R} = \frac{\Gamma_R(t)\, c_S^b}{\Gamma_S(t)\, c_R(r_o,t)} \tag{S.8}$$

$$\xi = \exp\left(\frac{nF}{RT}(E - E_s)\right) = \frac{\Gamma_O(t)}{\Gamma_R(t)} \tag{S.9}$$

where c_i^b and Γ_i stand for the bulk and surface concentrations of species i, respectively; $\Gamma_i^{\max}$ for the surface concentration of a full monolayer of i, r_o for the electrode radius, D_R for the diffusion coefficient of R and n for the number of electrons exchanged per molecule in the redox step. It has been assumed that $\Gamma_S^{\max} = \Gamma_O^{\max} = \Gamma_R^{\max}$. The applied potential E varies with time according to:

$$E = \begin{cases} E_d & t \le t_d \\ E_d - v(t - t_d) & t_d \le t \le t_r \\ E_d + v(t + t_d - 2t_r) & t_r \le t \end{cases} \quad \text{(S.10)}$$

where E_d stands for the deposition potential, t_d for deposition time, v for the scan rate and t_r for the time at which the potential scan is reversed.

The faradaic current i is given by:

$$i = nFA\frac{d\Gamma_O}{dt} \quad \text{(S.11)}$$

where A represents the electrode surface area.

The above boundary value problem was solved numerically by using the dynamic version of the spline orthogonal collocation technique described in a previous work.[1]

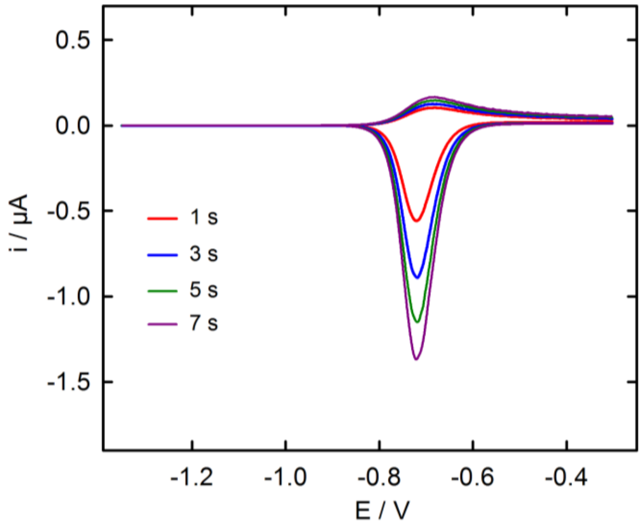

Fig. S4 Theoretical cathodic stripping voltammograms for reaction scheme S1 calculated for the indicated deposition times and the following parameter values: c_R^b = 5 μM, c_S^b = 55.5 M, v = 1V s^{-1}, E_d = -0.3 V, E_s = -1.1V, $K_{a,R}$ = 1x10^{-2}, D_R = 5x10^{-6} cm^2 s^{-1}, $\Gamma_R^{\max}$ = 8x10^{-10} mol cm^{-2}, r_o = 0.05 cm and T = 298 K

Fig. S1 shows a set of theoretical cathodic stripping voltammograms calculated for distinct deposition times, that mimic the experimental conditions described in this communication (Fig. 1). These calculations have been carried out by assuming a negligible adsorption of R, so that the forward cathodic wave displays the typical Gaussian-like shape for an immobilized species, whereas the backward anodic wave shows the typical shape for a diffusion-controlled oxidation. Under these conditions, the shape of the theoretical cathodic wave is insensitive to the actual values of Γ_i^{max}, E_s, $K_{a,R}$ and D_R. As a reference, to compare the experimental reductive desorption waves, a representative theoretical waveshape for the stripping of 25 pmol cm^{-2} of O has been calculated by using c_R^b = 5μM, c_S^b = 55.5 M, r_o = 0.046 cm, v = 1 V s^{-1}, T = 298 K and the arbitrary values of $\Gamma_R^{\max}$ = 8x10^{-10} mol cm^{-2}, D_R = 4.5x10^{-6} cm^2 s^{-1}, $K_{a,R}$ = 1x10^{-2}, E_s = -0.987 V, and t_d = 3.2 s. This theoretical wave can then be superimposed to the experimental ones by matching their peak potentials (solid lines in Figs. 2, 3 and 4 of the manuscript).

3. References

1 J. J. Calvente, R. Andreu, M. L. A. Gil, L. Gonzalez, A. Alcudia and M. Dominguez, *J. Electroanal. Chem.*, 2000, **482**, 18-31.