

Selective Binding of Divalent Cations at the Surface of Self-Assembled Monolayers of an Aromatic Bifunctional Molecule Studied on a Quartz Crystal Microbalance

Murali Sastry,* Vijaya Patil, and K. S. Mayya

Materials Chemistry Division, National Chemical Laboratory, Pune 411 008, India

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Self-assembled monolayers (SAMs) of a small aromatic bifunctional molecule, 4-carboxythiophenol, formed on gold films have been used to selectively bind Cd^{2+} and Pb^{2+} ions at the surface of the SAMs. SAMs formed with this molecule on Au have a surface rich in carboxylic acid functionality which can be used to bind the above-mentioned cations through an ion-exchange process. The kinetics of ion exchange, as well as the pH dependence of the binding of Cd^{2+} and Pb^{2+} ions on the SAM surface, have been followed using quartz crystal microbalance measurements. It is found that, at low pH where the carboxylic acid groups are expected to be unionized, significant mass increase is observed. At high pH, the percentage of ion exchange is found to be twice that expected from charge neutrality constraints (0.5 $\text{Cd}^{2+}/\text{Pb}^{2+}$ ion per carboxylic acid group). This is tentatively explained as being due to incorporation of $\text{Cd}(\text{OH})^+$ and $\text{Pb}(\text{OH})^+$ ions. The titration curve obtained yields an equilibrium binding constant of ~ 5.3 for both ions, which is close to that obtained for these ions in Langmuir monolayers and Langmuir–Blodgett multilayer films.

Introduction

Important advances in the understanding of producing self-assembled monolayers (SAMs) using a range of molecules transferred from solution onto solid supports have been motivated primarily by their technological potential.^{1–3} Tailoring of the terminal functionality of SAM-forming molecules through the use of *bifunctional* molecules has led to the interesting possibility of engineering the SAM surface. Some of the more exciting applications of such tailored SAMs include the adsorption of monolayers of clusters by immersion of the SAM in suitable colloidal solution,^{4–7} by imparting pH-dependent ion recognition capability to Au electrodes,⁸ and by building self-assembled multilayers using selective ionic interactions,^{9,10} to name a few. On a more fundamental level, the process of biomineralization¹¹ can be mimicked using SAMs with a suitably tailored surface functionality.¹²

Study of the interaction of charged organic surfaces and counterions in the aqueous medium is an important prerequisite for understanding processes relating to ion transport in biological membranes and selective ionic interactions^{8–10} as well as nucleation and growth of crystals at organic surfaces.^{11,12} It is well-known that the presence of counterions at the Langmuir monolayer–aqueous subphase interface critically affects the properties of built-up Langmuir–Blodgett (LB) films,¹³ and much effort has been directed toward understanding these interactions at the air–water interface.^{14–16} The replacement of the proton in the surface carboxylic acid group of molecules in Langmuir monolayers, as well as in SAMs with cations, (counterions) may be viewed as an ion-exchange process. The principle of ion exchange is quite general and is known to occur in many common clays, soils, minerals, and zeolites.¹⁷ This principle has been used in our laboratory to exchange cations (Pb^{2+} and Cd^{2+}) in Langmuir–Blodgett films¹⁸ and has been developed further to yield organized lamellar structures of thermally evaporated fatty acid films *via* cation exchange through immersion in suitable electrolytes.¹⁹ The literature concerned with the interaction of carboxylic acid functionalized

SAMs with counterions in solution is rather scarce, with the *in-situ* X-ray reflectivity studies of Scoles *et al.*¹² being the most detailed report. The X-ray photoelectron spectroscopy (XPS) studies of Cu^{2+} incorporation in self-assembled multilayer films of mercaptoalkanoic acids of Evans *et al.*,¹⁰ while not probing ionic interactions in solution, have provided important information on the oxidation state of the counterion in the films.

In this paper, we present results of our study on the counterion-binding properties (cation exchange) of carboxylic acid-terminated SAM surface of an aromatic bifunctional molecule, 4-carboxythiophenol, on Au films. Quartz crystal microgravimetry (QCM) performed *ex situ* has been used to investigate the pH-dependent counterion–surface interaction of Cd^{2+} and Pb^{2+} ions as well as the kinetics of ion binding to the SAM surface.

Experimental Details

The synthesis of the bifunctional molecule used in the formation of the SAM of this study has been described in an earlier work.⁷ Thin films of Au (≈ 2000 Å thick) were vacuum deposited in an Edwards coating system at a pressure of $\approx 10^{-7}$ Torr onto AT-cut quartz crystals. The AT-cut quartz crystals (6 MHz resonance frequency) were then immersed in a 10^{-3} M concentrated solution of the bifunctional molecule in absolute ethanol. On the basis of earlier studies on the kinetics of SAM formation with this molecule,⁷ a period of immersion of ≈ 3 –4 h was found to yield compact monolayers. The SAM-covered quartz crystals were then immersed in 10^{-4} M solutions of CdCl_2 and PbCl_2 maintained at different pH values, which were adjusted using ammonia and HCl.

The process of SAM formation, as well as the counterion binding to the SAM surface, was followed *ex situ* using an Edwards FTM5 quartz crystal microbalance with a frequency resolution and stability of ± 1 Hz. This yields a minimum detectable mass of ≈ 12 ng/cm², which is adequate for following the SAM formation as well as counterion binding at the SAM surface. Prior to measurement of the frequency changes in air after immersion in the salt solution, the quartz crystal was thoroughly washed with deionized water and dried. Frequency stabilization was found to occur within 15 min after washing,

* Author to whom correspondence should be addressed. Fax: 0091-212-330233. E-mail: SASTRY@NCL.ERNET.IN.

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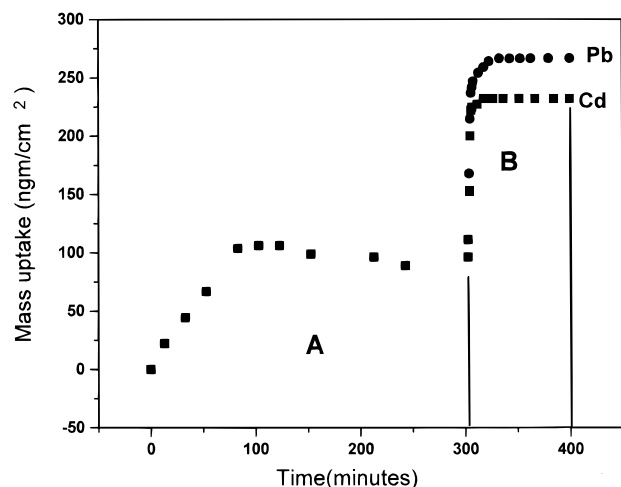


Figure 1. Kinetics of SAM formation on Au (region A) and Cd^{2+} and Pb^{2+} ion exchange after SAM formation (region B, subphase pH = 6) as measured by QCM.

which we attributed to adsorbed water evaporation from the quartz surface. Such time scales for drying have been observed by Roser and Lovell²⁰ in their QCM studies of highly charged multilayer LB films and have been explained as arising due to microscopic draining processes in the films.

Results and Discussion

Quartz crystal microgravimetry (QCM) is based on the principle of change in resonance frequency of an AT-cut quartz crystal on mass loading of the crystal surface. The frequency change can be simply related to the mass loading through the Sauerbrey equation:²¹

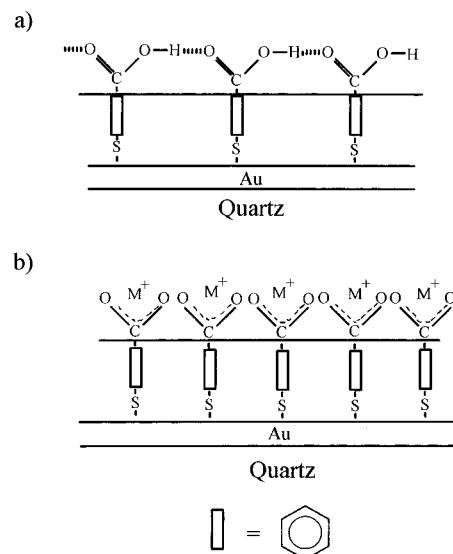
$$\Delta f = -2f_0^2 \Delta m / [A(\mu_q \rho_q)] \dots \quad (1)$$

where Δf is the frequency change corresponding to a mass loading Δm , A is the area of the electrode area (0.664 cm^2 in this study), μ_q is the shear modulus of quartz, ρ_q is the density of quartz, and f_0 is the crystal resonant frequency (6 MHz in this study). Due to its great sensitivity towards mass loading, QCM has emerged as one of the most important techniques for following the process of self-assembly on solid substrates.^{7,22,23}

The kinetics of SAM formation of the bifunctional molecule at room temperature was followed by QCM and have been dealt with in detail in an earlier report.⁷ The QCM mass uptake during SAM formation is shown as region A in Figure 1. The steady-state mass loading due to SAM formation is $\sim 100 \text{ ng/cm}^2$, which corresponds to a molecular area of 25 Å^2 . Due to the strong binding of the thiol group with the Au surface, the surface of the SAM is expected to be rich in carboxylic acid functionality,²⁴ with the carboxylic acid moieties forming hydrogen bonds with neighboring groups at low pH²⁵ as shown in Scheme 1a.

The surface carboxylic acid groups can be used to bind counterions as occurs in Langmuir–Blodgett films. This is shown in Scheme 1b as adsorption of a counterion M^+ . After the SAM was washed with absolute ethanol and thoroughly dried, the film-covered quartz crystal was immersed in 10^{-4} M concentrated CdCl_2 and PbCl_2 solution (electrolyte pH = 6), and the kinetics of ion exchange were followed using QCM. Figure 1 (region B) shows the mass uptake with time (frequency change was converted to mass loading using the Sauerbrey expression, eq 1) for the SAMs immersed in CdCl_2 (filled squares) and PbCl_2 (filled circles). It is seen from Figure 1 that, while compact SAM formation occurs over a time period

SCHEME 1



^a (a) Organization of SAM of the bifunctional molecule at low pH. (b) Counterion adsorption M^+ at the surface of the SAM at high pH.

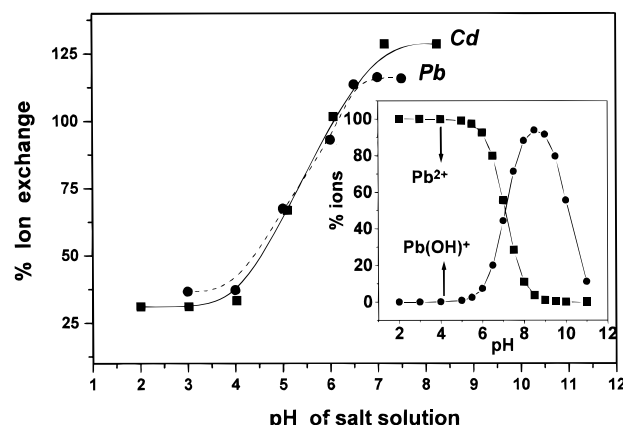


Figure 2. Percentage of ion exchange at the SAM surface as a function of electrolyte pH as determined from QCM mass uptake: filled circles, Pb ions; filled squares, Cd ions. Inset shows calculated percentages of Pb^{2+} and Pb(OH)^+ ions with electrolyte pH (details in text).

of $\sim 150 \text{ min}$, the binding of both Cd^{2+} and Pb^{2+} ions occurs much faster and an equilibrium mass loading occurs within 20 min of immersion. The bound ion monolayer is also extremely stable during prolonged immersion in the electrolyte.

In Figure 2, we show the percentage of ion exchange on the SAMs with electrolyte pH for immersion in both CdCl_2 and PbCl_2 solutions. The mass uptake was converted to percentage of ion exchange by determining the ratio $100 \times [\text{M}^{2+}/\text{COO}^-]$ ($\text{M} = \text{Cd}$ and Pb). In this scheme, 50% ion exchange would imply 0.5 M^{2+} ions per COO^- group, which is what is expected from charge neutrality constraints. The points shown in the figure refer to QCM measurements on different SAM films after immersion in the respective electrolyte. Repeated measurements on different SAMs at the various pH values showed not more than 10% variation in the ion exchange percentages demonstrated in the figure. Two interesting observations can immediately be made from Figure 2. The first is that the degree of ion exchange at high pH values is close to 130% for Cd^{2+} ions and $\sim 110\%$ for Pb^{2+} while, as explained above, the expected percentage for both ions based on charge neutrality is 50% (0.5 Cd^{2+} for every COO^- group). The second observation is that, at low pH values where the surface is expected to be completely unionized, significant mass uptake corresponding

to $\approx 35\%$ ion exchange occurs ($0.35 \text{ Cd}^{2+}/\text{Pb}^{2+}$ ion per carboxylic acid group). This result is totally at variance to those observed for LB films²⁰ and will be discussed below.

To our knowledge, this is the first report of the kinetics of ion exchange at modified SAM surfaces as well as their pH dependence. A careful examination of Figures 1 and 2 show that the ion-exchange process is initially extremely fast (a period of ≈ 5 min) followed by a slower exchange rate with complete exchange occurring within 20 min. This exchange time is close to that observed by us for cation exchange in multilayer Langmuir–Blodgett films as well as thermally evaporated fatty acid films.¹⁹ It is well-known that divalent cations such as those used in this study bind very strongly to ionized carboxylic acid groups both at the air–water interface as would be the case in Langmuir monolayers^{15,26–28} and on the surface of SAMs.¹² This strong binding of Cd^{2+} and Pb^{2+} to ionized carboxylate groups would explain the rapid ion exchange observed.

The degree of ion exchange observed both for Cd^{2+} and Pb^{2+} ions shown in Figure 2 is rather surprising. To recapitulate, we observe $\sim 130\%$ ion exchange for Cd^{2+} ions and $\sim 110\%$ exchange for Pb^{2+} ions at pH values greater than 6.4. In this regime, the carboxylic acid groups are expected to be completely ionized. On the basis of charge neutrality constraints, one would expect 50% exchange as mentioned earlier. In addition to this result, there is considerable mass uptake at pH values less than 4 where the carboxylic acid surface would be totally unionized. Structurally, there is close similarity between the carboxylic acid-functionalized SAMs of this study and Langmuir monolayers of fatty acids at the air–electrolyte interface, and it would be of interest to compare studies on such systems with ours.

Daillant *et al.*²⁸ have used grazing incidence X-ray fluorescence and reflectivity to study the interaction of Mn^{2+} ions with behenic acid Langmuir monolayers. They find that the number of Mn^{2+} ions per fatty acid molecule is 0.47 as expected in addition to the fact that the Mn^{2+} ions are localized in a very thin layer adjacent to the hydrophilic group of the fatty acid molecule. In their study of the structure of cadmium arachidate Langmuir monolayers by synchrotron X-ray diffraction and reflectivity, Als-Nielsen *et al.*^{16b} observed a counterion to carboxylic acid ratio of 1:1 (100% exchange, using our terminology) for Cd^{2+} ions at a pH = 8.8. This was explained as being due to a $\text{Cd}(\text{OH})^+$ complex being formed, which then interacts with the charged carboxylic acid group. Dutta *et al.*²⁶ infer a similar 1:1 ratio of Cu^{2+} to heneicosanoic acid in Langmuir monolayers at high pH values using X-ray diffraction measurements. In this context, the QCM work of Roser and Lowell²⁰ on Cd^{2+} ion inclusion in LB multilayers of docosanoic acid may be mentioned. They observed that the Cd^{2+} ion percentage at pH = 6.5 was 50% as expected with a small reduction in the area per molecule after ion incorporation as compared to the unionized acid molecule. Their measurements did not extend to the higher pH values used by other workers where 100% exchange was observed.^{16b,26}

Recently, Scoles *et al.*¹² have presented results on *in-situ* X-ray reflectivity studies of the Cd^{2+} , Pb^{2+} and Ca^{2+} counterion adsorption at the surface of SAMs of carboxylic acid-terminated alkanethiols, and we discuss these results in greater detail since they parallel our measurements to a large extent. Scoles *et al.*¹² found that the counterion concentration was highly localized close to the carboxylic acid group (≈ 1 ML thickness) indicating chemical interaction of the counterions with the carboxylic acid groups rather than purely electrostatic binding which would yield a double layer of larger thickness.¹² This has also been observed by other researchers.^{16b,20,26} For this reason, we believe that it would not be out of place to compare our *ex-situ* QCM

measurements with the *in-situ* reflectivity measurements of Scoles *et al.*¹² The electron density profiles obtained from the X-ray reflectivity studies performed as a function of varying electrolyte pH showed marked changes near the carboxylic acid terminal group. At low pH (pH = 3.9), they calculated a Cd^{2+} ion-exchange ratio of 0.58 per carboxylate group but explained that the calculated electron density could easily be accounted for by the presence of water and need not necessarily be due to the Cd^{2+} counterions. At this pH, the carboxylic acid groups are expected to be unionized and this is a reasonable assumption. However, the large mass increase observed by us (corresponding to $\sim 0.25 \text{ Cd}^{2+}/\text{Pb}^{2+}$ per carboxylate group, $\sim 25\%$ in Figure 2) at pH = 4 and below measured *ex situ* for both Cd^{2+} and Pb^{2+} cannot be attributed to adsorbed water. The quartz crystal frequency was extremely stable in air with no measurable change with time. As mentioned earlier, care was taken to thoroughly rinse the crystal with water before measuring the crystal frequency. This result is not interpretable by us at this stage and, as mentioned earlier, was observed in separate measurements on different SAM films.

As the solution pH was increased, Scoles *et al.*¹² observed an increase in the electron density near the terminal group and calculated the effective ion concentration. They observed that, at pH = 6.4, there was one Cd^{2+} ion per carboxylic acid group which was explained as being possibly due to binding of $\text{Cd}(\text{OH})^+$ ions. The reflectivity measurements were found to be similar for Pb^{2+} counterions with the small difference that the 1:1 overlayer formed at pH = 7 as compared to forming at pH = 6.4 for Cd^{2+} ions. Further increase in pH to beyond 8 showed a large increase in Cd^{2+} ion concentration to 1.39 ions/carboxylic acid group (corresponding to $\sim 140\%$ in our terminology). This additional electron density was explained as arising due to multilayer formation of $\text{Cd}(\text{OH})_2$. The percentage of ion exchange observed by us for both the ions studied agrees remarkably with those calculated by Scoles *et al.*¹² On the basis of comparison of our results with those of Scoles *et al.*,¹² we interpret a similar mechanism for the large mass increase at high pH values. This interpretation is strengthened based on a calculation of the various metal ion–hydroxide complexes in solution as a function of electrolyte pH using the stability constants tabulated in ref 29. The inset of Figure 2 shows results of such a calculation for the complexes of Pb^{2+} ions with electrolyte pH. It is clearly seen that, above pH = 7, the ion concentration is almost completely due to $\text{Pb}(\text{OH})^+$, which would explain the $\sim 110\%$ ion incorporation observed. A similar calculation can be shown for Cd^{2+} ions as well. A closer look at Figure 2 shows that, for the SAMs of this study, 100% exchange occurs at above pH = 6. The discrepancy between calculation and experiment may be due to the fact that the surface pH is expected to be different from that of the bulk pH which is used in the metal–hydroxide complex calculation.

While such calculations on cation complexes in solution can assist in an understanding of their binding at charged surfaces, direct spectroscopic evidence such as that provided by XPS is invaluable. Using XPS, Evans *et al.*¹⁰ have shown that Cu ions in self-assembled multilayer films grown by selective ionic interactions are incorporated while in the Cu^{2+} state. They observed further that Cu^{2+} rapidly gets reduced to Cu^+ due to exposure to photoelectrons. Preliminary XPS studies of Cd^{2+} and Pb^{2+} incorporated SAMs of the molecule of this study (ion incorporation at pH = 7) indicate the presence of a hydroxide metal complex. A detailed analysis of the XPS investigation will be presented elsewhere.³⁰

There are however some differences in the nature of variation of mass uptake with electrolyte pH as compared to the electron

density change observed in the work of Scoles *et al.*¹² We find that the takeoff in the ion exchange occurs just above pH = 4 for both the ions, whereas in the X-ray reflectivity report, the takeoff occurs above pH = 5. The region of ion exchange increase with pH is from pH = 4 to 7 for the counterions of this study, whereas the stabilization occurs above pH = 6.4, followed by a further large increase above pH = 8 as observed by Scoles *et al.*¹² While the general form of the titration curve in both studies is similar, the above are the main points of deviation.

Roser and Lovell²⁰ have investigated Cd²⁺ ion inclusion into Langmuir–Blodgett multilayer films of docosanoic acid as a function of the electrolyte pH. While they observe an ion exchange maximum of ~0.5 Cd²⁺ ion per carboxylic acid group, the nature of the variation in percentage ion inclusion is quite similar to what has been observed by us. To be more specific, the takeoff in increased frequency occurs at just above pH = 4 and stabilizes above pH = 6. The equilibrium binding constant pK for the Cd²⁺ and Pb²⁺ ions estimated from Figure 2 is ~5.3 and is in good agreement with that reported by Roser and Lovell (pK = 5.35).²⁰ Roser and Lovell mention that the pK value obtained for Cd²⁺ ions in LB films agrees with the equilibrium binding constant obtained from X-ray reflectivity studies performed on Langmuir monolayers at the air–water interface³¹ which indicates similar binding of the counterions both in LB multilayers and in monolayers. The pK_A value of benzoic acid which is closest to the molecule of this study is ~4.2³² while that of a long chain fatty acid is ~5.76.³³ Another factor which must be considered is the role of the thiolate bond formation with the metal surface on the pK_A value mediated by the delocalized π electrons. Taking these factors into account, the agreement of the equilibrium binding constants for Cd²⁺ obtained by us and those reported for long chain fatty acids is surprising. Further work on ion exchange with different divalent cations as well as mono- and trivalent cations on SAMs of the same bifunctional aromatic molecule, as well as fractionation of two or more counterions in solution, is in progress to clarify the above point.

There is one common point which connects the X-ray reflectivity work on Langmuir monolayers,^{16b,28} X-ray reflectivity on SAM surfaces,¹² and the QCM results presented in this paper which needs to be highlighted. Als-Nielsen *et al.*^{16b} have shown that, depending on whether NaOH or ammonia is used to alter the CdCl₂ subphase pH, the stoichiometry of the counterion to amphiphilic molecule can be 1:2 (counterion binds as Cd²⁺) or 1:1 (counterion binds as Cd(OH)⁺), respectively. Interestingly, ammonia was used to alter the pH in the study of Scoles *et al.*¹² and this study with a similar 1:1 ratio obtained for Cd²⁺ binding at SAM surfaces as determined from X-ray reflectivity or QCM measurements. In the study of pH dependence of Mn²⁺ adsorption at fatty acid Langmuir monolayers, NaOH was used for alteration of the subphase pH, where it may be recalled that a 1:2 stoichiometry was calculated.²⁸ No statement on this aspect can be made regarding Roser and Lovell's QCM work since it was not mentioned how the pH was altered.²⁰

To summarize, pH-dependent cation binding to SAM surfaces of 4-carboxythiophenol has been studied using quartz crystal microgravimetry. The pH dependence of the ion binding is similar to that observed in LB films and Langmuir monolayers.

The degree of exchange at high pH values is twice as large as that expected from charge neutrality considerations, indicating chemical attachment as M(OH)⁺, and agrees with X-ray reflectivity measurements of a similar bifunctional SAM.¹²

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