INTERACTIONS OF CADMIUM IONS WITH CARBOXYLATE-FUNCTIONALIZED SELF-ASSEMBLED BILAYERS:
IN SITU ATR-FTIR STUDIES

Ionel C. Stefan[*], Daniel Mandler[o] and Daniel A. Scherson[*]

[*]Department of Chemistry
Case Western Reserve University, Cleveland, OH 44106

[o] Department of Inorganic and Analytical Chemistry,
The Hebrew University of Jerusalem,
Jerusalem 91904, Israel

INTRODUCTION

Functionalized bilayers are currently being examined in our laboratory as biomimetic membranes and as versatile structured interfaces for detection and binding of metal ions from solution using judiciously selected terminal groups to impart the desired selectivity.(1) The primary focus of this work is to monitor interactions of self-assembled bilayers (SABs) bearing carboxylic functionalities with solution phase Cd^{2+} by ATR-FTIR. Divalent metal ions, e.g. Cd^{2+}, are well known to strongly interact and stabilize interactions with fatty acid Langmuir-Blodgett (LB) monolayers at the air/water interface.(2) Measurements were performed both as a function of Cd^{2+} concentration and pH to gain insight into the competing effects due to the polyelectrolyte characteristics of the bilayer itself.

EXPERIMENTAL

The sequential self-assembly of octadecyl trichlorosilane (OTS) and palmitic acid (PAL) layers on Ge was performed using a method described in detail elsewhere,(4) while monitoring the intensity of the IR features of OTS and PAL in the ATR mode using a Brucker FTIR spectrometer. Interactions of Cd^{2+} ions with the terminal $COOH/COO^-$ groups were investigated by injecting aqueous solutions of $Cd(ClO_4)_2$ in the ATR cell. Measurements were performed in 10 mM $HClO_4$ aqueous solutions with the pH adjusted to the desired value with 0.1 M NaOH in the range 2 – 6.

RESULTS AND DISCUSSION

Shown in the upper panel Fig. 1 are spectra of an OTS monolayer and PAL/OTS bilayer nitrogen dried from pH 7.4 and pH 2 solutions, using the spectrum of bare Ge, as a reference. Differences in the packing structure of the layers, as a function of pH could be extracted from the position of the CH_2 scissoring band, $\delta(CH_2)$, at about 1470 cm^{-1}.(2,3) In analogy with results obtained for Langmuir-Blodgett monolayers of fatty acids at the water/air interface, the SAB prepared in this work are packed in an hexagonal lattice when dried from pH 2 and triclinic from pH 7.4 solutions, respectively.

No significant specific interactions between Cd^{2+} and $COOH/COO^-$ terminal groups could be detected for pH < 4, as evidenced from the data in the middle panel, in which the spectra of the SAB is referenced to spectra obtained in a Cd^{2+}-free solution at the same pH. However, the presence of Cd^{2+} ions at a concentration of 1μM seems to affect the layer packing at all pH values, as seen by the increase in the intensity of the methylene stretching ($\nu_a(CH_2)$ and $\nu_s(CH_2)$) and scissoring peaks ($\delta_a(CH_2)$), at ca. 2917, 2550, and 1470 cm^{-1}, respectively. Moreover, the shift in the position of these peaks to lower energies at higher pH values in the presence of Cd^{2+} ions indicates an increase in the packing density. This process is partly reversible, as seen in the upper spectrum of the series, which show that the stretching band peaks return to their initial value of 2917.3 and 2850.3 cm^{-1}. Their presence, however, reveals that a certain degree of order imposed by the presence of Cd^{2+} remains after its removal at low pH.

The specific interaction of Cd^{2+} with the terminal $COOH/COO^-$ groups is apparent at pH > 4 by the $\nu_a(COO)$ and $\nu_s(COO)$ at ca. 1539 and 1411 cm^{-1}. However, These peaks completely disappeared after injection of a pH 2 solution.

The dependence of Cd^{2+}-SAB interactions on Cd^{2+} concentration was studied at pH = 6. The results are shown in the lower panel, where spectra for a given concentration, denoted by the same type of line, indicate data obtained at 20 min intervals, going upward in the series. As evidenced from these data, the appearance of three different bands in the 1500-1650 range at higher Cd^{2+} concentrations, is consistent with the presence of three different types of Cd-COO interactions, i.e. bidentate, bridging and ionic.(5) The results suggest that the packing of carboxylic SAB at pH 6 is high, and comparable to LB layers of the same acid compressed to about 22 Å^2/molecule.(2)

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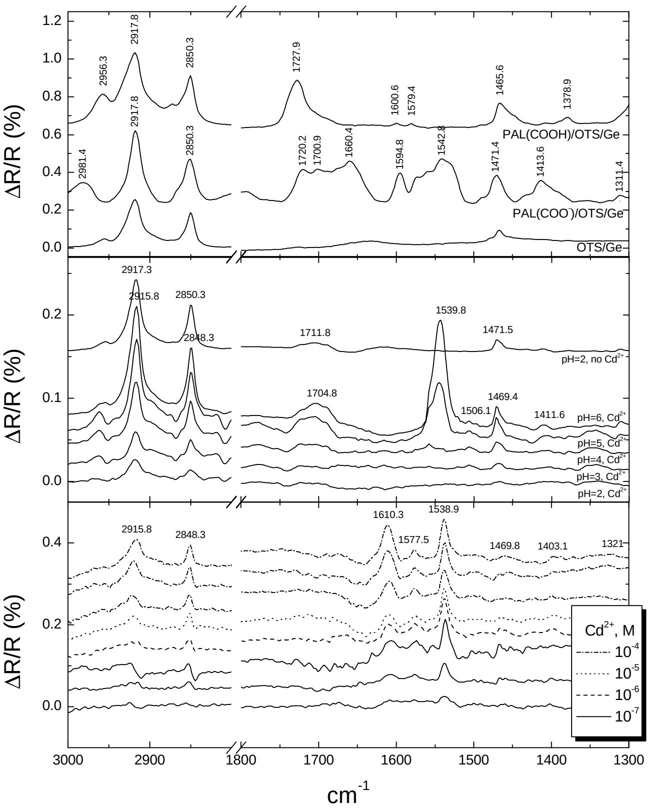

Fig. 1. OTS SAM and PAL/OTS SAB spectra (upper panel); pH (middle panel) and concentration (lower panel) dependent spectra of Cd^{2+} interactions with PAL bilayers.

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