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# METAL-ION ADSORPTION ON CARBOXYL-BEARING SELF-ASSEMBLED MONOLAYERS COVALENTLY BOUND TO MAGNETIC NANOPARTICLES

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## INTRODUCTION

Procedures have been developed and implemented for the preparation and characterization of well-defined, 11-undecanoic acid SAM bearing carboxyl terminal groups, covalently-bound through siloxane groups to commercial superparamagnetic magnetite particles. The synthetic approach relies on the hydrolysis of chlorosilane functionalized species on the partially hydroxylated oxide surface, leading to the formation of a polymeric network of siloxane chains bound to the underlying substrate.<sup>1</sup> Evidence for the closed-packed nature of the SAM examined in this work was obtained by direct titration<sup>2</sup> of suspensions in aqueous solutions for carboxyl-functionalized polymeric spheres. Furthermore, quantitative information regarding the affinity of these SAM for  $\text{Cd}^{2+}$  ions in aqueous solutions was obtained from measurements of the adsorption curves, using anodic stripping voltammetry under forced convection for quantitative detection and of solution phase  $\text{Cd}^{2+}$ .

## EXPERIMENTAL SECTION

11-(Trichlorosilyl) undecanoyl chloride (TUC) was synthesized according to the literature.<sup>1</sup> 11-UC-functionalized magnetite (11-UC- $\gamma\text{-Fe}_2\text{O}_3$ ) was prepared by adding 0.2 mmol TUC and 100 mL heptane to a 250 mL flask, followed by 310 mg  $\gamma\text{-Fe}_2\text{O}_3$  (99+%, Alfa). This mixture was then agitated in an ultrasonic bath for 2h at room temperature. The 11-UC- $\gamma\text{-Fe}_2\text{O}_3$  particles were magnetically confined and subsequently washed with heptane and dilute NaOH (pH = 9-10) three times to afford the particles as free flowing powder. The surface density of carboxylic groups on the 11-UC- $\gamma\text{-Fe}_2\text{O}_3$  particles was determined by titration of deaerated ( $\text{N}_2$ ), well-stirred solutions of 8 mL NaOH (9.13 mM) in 50 mL water before and after addition ca. 20 mg 11-UC- $\gamma\text{-Fe}_2\text{O}_3$  particles. The NaOH concentration was determined using HCl (9.78 mM) standardized by sodium carbonate (ACS certified, 99.8%). pH values were read with a pH electrode (Chemcadet, Model 5984-50) immersed in the solution following addition of HCl aliquots from a regular buret. The extent of  $\text{Cd}^{2+}$  adsorption on 11-UC- $\gamma\text{-Fe}_2\text{O}_3$  particles was determined by anodic stripping voltammetry using a glassy carbon (GC) rotating disk electrode (RDE, Pine Instruments) in a 100 mL three-neck round bottom flask. The deposition step was performed with the RDE rotating at 2500 rpm for 60 s, at which point the rotation was stopped, and the potential then scanned linearly between -1.0 and 0.0 V vs SCE at a rate of 5 mV/s.

## RESULTS AND DISCUSSION

Shown in upper panel Fig. 1 are titration curves of a 9.13 mM NaOH solution obtained in the absence (open circles) and in the presence of 15.4 mg 11-UC- $\gamma\text{-Fe}_2\text{O}_3$  particles (solid circles), where the dotted and solid

lines represent, respectively, best fits to the experimental points using arbitrary functions. As clearly indicated by the corresponding derivative curves in the lower panel in this figure, addition of the particles yielded two well-defined inflection points, from which the total amount of surface carboxylate was estimated to be  $2.10 \times 10^{-4}$  mol carboxylate/g 11-UC- $\gamma\text{-Fe}_2\text{O}_3$  particles. Based on the average  $\gamma\text{-Fe}_2\text{O}_3$  particle diameter reported by the manufacturer, i.e. 20-30 nm, the surface density of carboxylate groups, ca.  $10^{14}$  molecules/ $\text{cm}^2$ , is of the same order of magnitude as that of closed-packed alkane chains SAM on solid supports reported in the literature. Plots of  $Q$  (see left ordinate) vs  $[\text{Cd}^{2+}]_{\text{fin}}$ , where  $Q$  is the amount of adsorbed  $\text{Cd}^{2+}$  in mmol per g of 11-UC- $\gamma\text{-Fe}_2\text{O}_3$  vs  $[\text{Cd}^{2+}]_{\text{fin}}$  for 0.1 M  $\text{NaClO}_4$  in 10 mM MOPS buffer solutions at pH = 7 containing 20 mg 11-UC- $\gamma\text{-Fe}_2\text{O}_3$  particles obtained for two separate trials are shown by the open and solid circles in Fig. 2. The same results, but in terms of mole ratio of  $\text{Cd}^{2+}$ /surface carboxylic groups vs  $[\text{Cd}^{2+}]_{\text{fin}}$  are given by the right ordinate in this figure. Based on the results obtained for  $[\text{Cd}^{2+}]$  ca.  $3 \times 10^{-4}$  M, the ratio of  $\text{Cd}^{2+}$ /total -COOH groups (see right ordinate, Fig. 2) is 1:2, which corresponds to full charge balance.

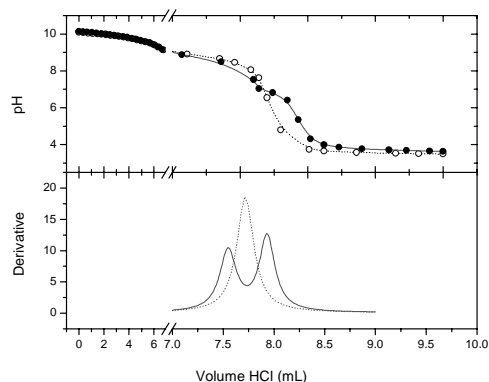


Figure 1. Titration curve of a NaOH solution of unknown concentration in the presence (solid line, solid circles) and in the absence (dotted lines, open circles) of 20 mg of UC- $\text{Fe}_2\text{O}_3$  particles using an HCl solution as a titrant (upper panel). The corresponding derivatives are shown in the lower panel in this figure.

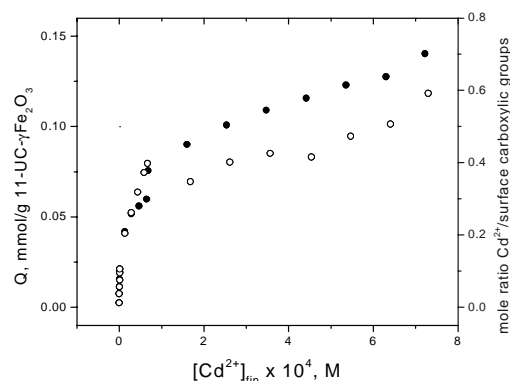


Figure 2. Plots of  $Q$  (see left ordinate) vs  $[\text{Cd}^{2+}]_{\text{fin}}$ . See text for details.

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