

Use of Atomic Force Microscopy Force Measurements To Monitor Citrate Displacement by Amines on Gold in Aqueous Solution

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Using an atomic force microscope, the adsorption of 4-(dimethylamino)pyridine and pyridine, in aqueous solution, onto trisodium citrate equilibrated gold has been monitored by the decrease in the electrostatic potential of the gold surface with time. Pronounced changes in the force–separation curves as a function of time were observed, with determined potential decreases in the range of 20–30 mV. The time dependent diffuse layer potentials changes have been attributed to the displacement of citrate ions on the gold surface by the more strongly adsorbing aromatic amines.

Introduction

In previous studies we have demonstrated that the atomic force microscope (AFM) is capable of making accurate force measurements between hard, charged surfaces in which the potentials of the isolated surfaces do not change while the experiment is underway.¹ In addition, several workers from this group have looked at the effect adsorbed charged species have on the electrostatic properties of the surfaces.^{2–4} In this paper, we extend this work and show that the AFM can collect accurate time dependent force data; i.e., measurements can be conducted on a system that has changing values of potential and charge with time.

The system chosen for this investigation was the displacement of charged citrate ions from the surface of gold by uncharged pyridine and a pyridine derivative. Previous electrophoresis studies, on this system, have shown that the addition of pyridine or 4-(dimethylamino)pyridine (DMAP) can substantially lower the potential of gold particles stabilized with citrate ions.⁵ All the sols studied had a negative electrophoretic mobility, thought to be due to the presence of specifically adsorbed citrate anions. Other evidence to support this assumption comes from the observation of the surface-enhanced Raman spectrum (SERS) of citrate adsorbed on gold particles.⁶ The mobility of the gold sol studied decreased from $-4.5 \mu\text{m s}^{-1}$ per V cm^{-1} to $0 \mu\text{m s}^{-1}$ per V cm^{-1} upon the addition of 5×10^{-3} M DMAP. This reduction in mobility was explained by the displacement of negative citrate ions on the surface by uncharged DMAP molecules. SERS studies

have revealed that DMAP (and pyridine) adsorbs onto the surface of gold.^{7,8}

Experimental Section

Materials. The gold flat surfaces were made from glass microscope slides cut into squares 1 cm^2 . These samples were first coated with a 10 nm layer of chromium and then a layer of gold no less than 50 nm thick. V-shaped silicon nitride cantilevers with tungsten spheres ($5\text{--}10 \mu\text{m}$ diameter) attached were sputter coated with 20 nm of gold. All gold-coated surfaces were kept in clean, covered petri dishes in a laminar flow hood and rinsed with AR grade ethanol and blown dry with nitrogen before use.

4-(Dimethylamino)pyridine (DMAP) (*N*-(4-pyridyl)dimethylamine), pyridine and trisodium citrate, all AR grade, were used as received from the commercial suppliers.

Force Measurements. The force measurements were taken with a Digital Instruments, Inc., Nanoscope III atomic force microscope. The technique used to make these measurements is well documented.^{1–4,9} The spring constant of the cantilevers used in these experiments was determined by the method of Cleveland *et al.*¹⁰ The short wide-legged triangular cantilever had a spring constant of $0.18 \pm 0.02 \text{ N m}^{-1}$.

Analysis. All interaction data were fitted with DLVO theory.^{1–4,9} When AFM measurements are taken between a colloidal sphere, radius ($R > 1 \mu\text{m}$), and a flat plate, the Derjaguin approximation can be used to relate the interaction free energy per unit area between parallel plates to the force (F) between the sphere and the flat surface¹¹

$$F/R = 2\pi(V_A + V_R)$$

Here V_A is the van der Waals interaction free energy per unit area and V_R is the electrical double layer interaction free energy per unit area between two parallel flat plates. We have ignored the effect of retardation¹² on the van der Waals force.

The algorithm used¹³ to calculate the theoretical curves is only strictly correct for 1:1 electrolytes. As trisodium citrate is a 1:3 electrolyte, the diffuse layer potential we calculate using this method is only approximate. Theoretical Debye lengths were calculated from the concentration of sodium ions present; i.e., for solutions containing 5×10^{-4} M trisodium citrate the 1:1

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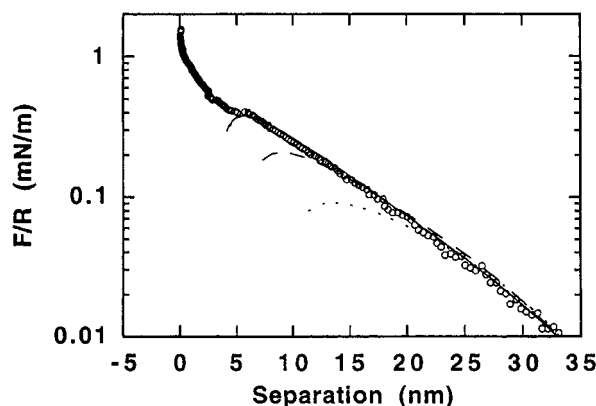


Figure 1. Normalized force–separation curve taken between gold surfaces in the presence of 5×10^{-4} M trisodium citrate. Constant charge curves only are shown. The fitting parameters are diffuse layer potential = -34 mV, Debye length = 8.2 nm (theory value 7.88 nm), and $A_H = 7 \times 10^{-20}$ J (full line); -38 mV, 10.9 nm, 2.5×10^{-19} J (dashed line); and -37 mV, 9.1 nm and 1.5×10^{-19} J (dotted line).

electrolyte concentration was assumed to be 1.5×10^{-3} M. The surfaces studied in this series of experiments were negatively charged so the counterion was the sodium ion. Although the trends predicted by this procedure should be valid, it should be remembered when reading this paper that we have made this approximation.

The change in surface concentration of citrate molecules should be closely related to the change in surface charge and, therefore, diffuse layer charge. For a symmetric electrolyte, of concentration c , in water at 25°C , the diffuse layer charge, σ_d , can be calculated from the diffuse layer potential, ψ_d ¹⁴

$$\sigma_d = 11.74 c^{1/2} \sinh(19.46 z \psi_d)$$

where ψ_d is in volts and σ_d is in $\mu\text{C cm}^{-2}$.

Method. Solutions containing the same background concentration of citrate dosed with the required amount of pyridine or DMAP were introduced into the cell through a syringe. The timer was started when the pyridine/DMAP solution was first introduced into the cell.

Results

Citrate Solutions. In 1×10^{-4} M trisodium citrate solutions, at ambient pH ~ 7.8 , the diffuse layer potential measured was $|42 \pm 5|$ mV. In 5×10^{-4} M citrate solutions, at pH ~ 8 , the fitted potential was $|33 \pm 2|$ mV. The sign of the potentials were assumed to be negative in accordance with microelectrophoresis results.⁵

In agreement with work by Biggs *et al.*,⁴ DLVO theory is not sufficient to completely describe the interaction between citrate-covered gold surfaces. As can be clearly seen in Figure 1 there is a non-DLVO short range repulsion present in the interaction curve. In the absence of citrate these short range forces are not observed for the gold–gold system.¹⁵

At a separation of ~ 6 nm (Figure 1) there is a slight turnover in the experimental data as if the surfaces were about to enter the primary minimum but were prevented by a short-range repulsive force. To fit this turnover in the force–separation curve, a Hamaker constant of 7×10^{-20} J is needed, much less than the 2.5×10^{-19} J fitted by Biggs and Mulvaney for bare gold surfaces.¹⁵ In Figure 1 we also show theoretical fits with different Hamaker constants.

A Hamaker constant of 7×10^{-20} J results in the best agreement with both turnover distance and Debye length.¹⁶

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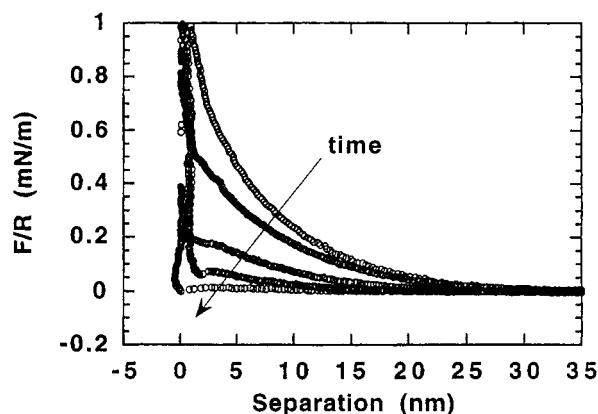


Figure 2. Normalized force–separation curves for the interaction between gold surfaces in the presence of trisodium citrate (1×10^{-4} M) and DMAP (1×10^{-3} M) at pH 10.5. After ~ 15 min the repulsion decreased until there was an attraction between the surfaces. Times after injection of DMAP for curves are 0, 2, 5, 9, and 14 min.

We attribute this to two reasons: (i) a loose network of citrate molecules (possibly held together by intermolecular hydrogen bonding) exists at each gold surface creating a steric/electrosteric barrier which prevents the surfaces from entering a primary minimum, and (ii) these adsorbed layers of citrate molecules lower the effective Hamaker constant the approaching surface “sees”. As the separation between the citrate-covered surfaces approaches the thickness of the citrate layers, the effective Hamaker constant acting on the two surfaces will tend toward that due to the adsorbed layers themselves.¹⁷

The choice of Hamaker constant has little effect on the diffuse layer potential derived for the system. There is only a 12% difference (-34 to -38 mV) in the fitted potentials using the different Hamaker constants. In effect this short-range behavior is ignored and only the long-range electrostatic repulsion data are taken into account.

Pyridine and DMAP Solutions. In Figure 2 we show the decrease with time of the strength of the repulsive force upon the addition of DMAP. The original solution was an ambient pH, 1×10^{-4} M sodium citrate solution. This solution was replaced with a pH 10.5, 1×10^{-4} M sodium citrate solution containing 1×10^{-3} M DMAP. The double layer repulsion between the surfaces was seen to decrease until the interaction became attractive after about 15 min.

Pyridine was seen to have the same effect of decreasing the electrostatic repulsion between the gold surfaces; see Figure 3. However, the interaction did not become attractive after the addition of pyridine but retained a repulsive component.

The rate of the decrease in diffuse layer charge was seen to be dependent on the concentration of DMAP. Keeping the background concentration of citrate constant, the rate increased as the concentration of DMAP increased. If we assume the displacement of the citrate ions by DMAP molecules follows a first-order rate law, we can plot the natural log of the diffuse layer charge versus time; see Figure 3. The diffuse layer charge, and therefore the surface charge, calculated is relatively low suggesting a low density of charged citrate on the gold surface.

(16) This is a different value than that used in the previous work presented in ref 4. In both cases the fitting procedure used is arbitrary, but this is because of the uncertainty of the adsorbed layer thickness. As we show here this uncertainty in the value of A_H used in the fit does not significantly affect the electrostatic potential calculated.

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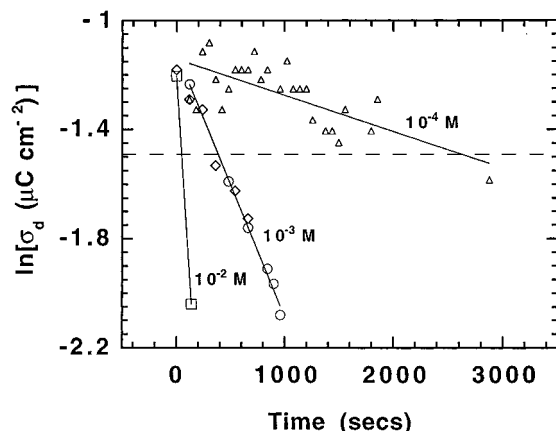


Figure 3. Change in diffuse layer charge with time and with differing concentrations of DMAP. Both pyridine, \diamond , and DMAP, \circ , are shown at 1×10^{-3} M concentrations. All solutions were at pH 10.5 and contained a background concentration of 1×10^{-4} M trisodium citrate. Each concentration data set, except pyridine, is a combination of two experiments. Lines drawn are best fits to the data. The gradients of the lines of best fit are, from lowest DMAP concentration to highest, $-1.32 \times 10^{-4} \text{ s}^{-1}$, $-9.15 \times 10^{-4} \text{ s}^{-1}$, and $-6.06 \times 10^{-3} \text{ s}^{-1}$. Dashed line represents charge due to a potential of -25 mV. The end potential reached by the two higher concentrations is -15 mV, and with 1×10^{-4} M DMAP the end potentials is -22 mV.

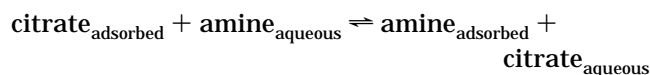
Although pyridine is a neutral molecule at pH 10.5, DMAP ($pK_a = 9.7^{18}$) exists as both neutral (86%) and as a positively charged species (14%). There is a possibility that some of the decrease in charge of the gold surface is not simply due to DMAP replacement of citrate ions but also due to charge neutralization by cationic DMAP adsorption. Raman studies on DMAP adsorption clearly show adsorption occurs but cannot distinguish which

species (neutral or cationic) is adsorbing. However, because the rate of charge decrease due to pyridine and DMAP adsorption is similar, see Figure 3, it is most likely that citrate ions are replaced by the aromatic amine not simply charge neutralization.

From the fits to the data presented in Figure 3, the rate of the decrease in diffuse layer charge was seen to increase by a factor of 7 as the concentration of DMAP was increased 10-fold. The noncorresponding increase in the rate with the increase in concentration of the amine may be due to effects arising from the multilayer structure of the adsorbed citrate.

Conclusions

The force measurements provide, for the first time, a direct measurement of the electrostatic changes occurring on a surface during the displacement of one surface adsorbed species (citrate) by another (pyridine + DMAP). Not only is the establishment of the equilibrium



able to be monitored but also the electrostatic changes on the interacting surfaces can be quantitatively determined during approach to equilibrium.

The use of the AFM in the manner described here should prove to be of value in studying the role of various solution additives in a variety of colloidal systems. Indeed, recent AFM work conducted on the reduction of AuCl_4^- by citrate shows that marked changes occur with reaction time on gold surfaces in contact with the solution.¹⁹ (These observations have a direct bearing on the behavior of colloid formation by the $\text{AuCl}_4^-/\text{citrate}$ method.²⁰)

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