# Molecular Approach to the Surface Potential Estimate of Thiolate-Modified Gold Nanoparticles

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The electrophoretic mobility is measured by a photocorrelation spectroscopic method to derive a  $\zeta$ -potential as a function of pH using gold nanoparticles with a well-defined surface. Since the Debye length,  $1/\kappa$ , of the dispersion ranges from 0.5 to 340 nm and the radius of a particle *a* is in nanometer scale, we use a recently developed formula (Ohshima, H. *J. Colloid Interface Sci.* **2001**, *239*, 587) for the estimate of  $\zeta$ -potentials which is applicable to wide  $\kappa a$  region. The  $\zeta$ -potentials derived are compared with those of theoretical ones in which we use only molecular parameters such as dissociation constants of mercaptosuccinic acid and given parameters such as a particle size, pH, composition of electrolyte in a dispersion, that means no adjustable parameters used. Qualitative agreement was attained between  $\zeta$ -potentials and surface potentials purely from theory.

#### Introduction

There is current interest in synthesizing and characterizing a gold nanoparticle with a self-assembled monolayer (SAM) surface both from a technological importance as a key substance in nanotechnology and from a scientific view of size-dependent properties. One of the most important parameters used to characterize a particle is the charge or the surface potential of particles. And yet the determination of the surface charge of nanoparticles and its theoretical derivation is still a challenging goal in colloid chemistry. Recent development for the SAM formation on gold nanoparticles has potential to address this formidable subject.<sup>1</sup> However, a quantitative calculation of the surface potential of a colloidal particle is still difficult because of the lack of the knowledge regarding the accurate surface structure of a particle if one wants to derive the potential using only a set of molecular parameters. What is a charging mechanism of a particle in a solvent and what determines the surface potential are thus still open questions. A lack of the methodology for accurate determination of the experimentally available surface potential is another problem. We often use an experimentally derived  $\zeta$ -potential instead of a surface potential, and yet, a method of accurate determination of  $\zeta$ -potential from electrophoretic mobility is a current interest.<sup>2</sup> Although the electric double layer masks the true feature of surface charges of a particle, systematic examination of the behavior of the particle under the external electric field may enable us to solve the question of what is the surface potential.

The profound understanding of the surface potential of a nanoparticle may bridge over the valley between the charge concept of ions (the radius of curvature is very small) and the surface potential concept of solid plates (the radius of curvature is infinite) in electrolytic solution. That is to say, nanoparticles should be a good test material to this goal. Since the development of the synthesis of surface-modified nanoparticles with thiolate, it is possible to characterize the surface state in a molecular level.<sup>3</sup> The surface of SAM particles is ideally molecularly homogeneous and thus their surface state can be described in a molecular level. If so, we can derive the surface potential solely by molecular parameters of surface modifiers. To address this object, the following conditions must be satisfied.

(1) Knowledge of an accurate surface structure. One guarantees the SAM structure using mercaptosuccinic acid (MSA) molecule as a surface modifier. All the analytic methods including elemental analysis, thermogravimetric measurement, and FTIR showed that the particles can be regarded as molecules.<sup>4</sup> Briefly, the occupation area per MSA molecule on gold for 2 nm-particles, 0.156 nm<sup>2</sup>, is an average of (100) and (111) surfaces which is directly identified by recent STM microscopy.<sup>5</sup>

(2) Homogeneity of particle ensemble. Homogeneity of the particle system is proved by the crystallization of particles as reported by a recent paper.<sup>6</sup> If particles are not uniform in size, shape, and surface species, crystallization of particles is impossible. The success of crystallization suggests that the particles can be regarded as if it were a molecule.<sup>7</sup>

(3) The system should be as simple as possible to bear the analytic evaluations. Ideally, the system should consist of only particles and their counterions. It is a standard procedure to use a solution with supporting electrolyte to maintain the constant ionic strength preventing pH fluctuation caused by unintended spurious contamination such as dissolution of carbon dioxide and so forth or avoiding disturbance in adsorption—desorption equilibrium. Hence, the above requisite contradicts the standard condition in which the composition of solution becomes more

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or less complex. However, instead, we expect a large surface potential at very low ion concentration that is realized in the simple system.

When we have ideal particles whose surfaces are molecularly clarified and have a sharp size distribution, all requisites from (1) to (3) are satisfied. To date, it is not easy to get ideal particles. But recent developments in crystallizing nanoparticles encourage us to attempt to this goal. In this report, we try to derive the surface potentials of nanoparticles with MSA using no fitting parameters and compare them with experimentally obtained  $\zeta$ -potentials. The present paper is, to our knowledge, the first attempt to test existing theories, which predict the surface potential of particles and plates with no adjustable parameters, using a nanoparticle whose surface is characterized in molecular level enabling theoretical calculation of the potential.

### **Experimental Section**

**Chemicals.** All the chemicals in this research are of reagent grade and used as received. Hydrogen tetrachloroaurate tetrahydrate (HAuCl<sub>4</sub>•4H<sub>2</sub>O, 99%), mercaptosuccinic acid (HOO-CCH<sub>2</sub>CH(SH)COOH, 97%), citric acid monohydrate (HOOC-CH<sub>2</sub>C(OH)(COOH) CH<sub>2</sub>COOH•H<sub>2</sub>O, 99.5%), methanol (99.8%), ethanol (99.5%), and hydrochloric acid solution containing 36% HCl were from Wako Pure Chemical Co. Sodium hydroxide (95%) was from Kanto Chemical Co. Distilled water of high resistivity > 18.0 M $\Omega$  cm was used just after distillation to make a sample suspension.

**Particle Synthesis and Surface Modification.** Gold nanoparticles were prepared according to the established method.<sup>8</sup> Briefly; 106 mL of 2.2 mM sodium citrate was brought to boil for 10 min and 1 mL of 24.3 mM HAuCl<sub>4</sub> was added under vigorous stirring. After the color of the solution changed to red for about 3 min, the solution was boiled for the next 15 min and then left to cool. The formal reaction of this process is expressed as follows:

Eighty milliliters of the cooled solution was then mixed with 80 mL of 6 mM (largely excess amount) mercaptosuccinic acid aqueous solution for 90 min, then sealed into a Visking tube (30/32), and dialyzed against distilled water. We needed 5-daysdialysis with two times exchange of water per day during dialysis until there was no smell of sulfur from free mercaptosuccinic acid. The byproduct, HCl, was also removed during this process. The final pH of the solution was 5.8. After dialysis, the UV bands in the absorption spectra which are originated from citrate or mercaptosuccinic acid disappeared showing that pure carboxylate-modified gold particles were formed (Figure 1, compared c to a or b). We have made many preparations, because, as stated in the next paragraph, fresh sample dispersions were needed for the every pH reading and mobility measurements to avoid any unintended exogenous contamination. These particles have a mean diameter in the range 15~25 nm for the different lots, 24 nm for the majority. The number of MSA molecules per single particle is calculated to be 8500 for the size of a 24-nm particle .

**pH Titration.** Hydrochloric acid was used in the acidic region to change the pH of the dispersion and sodium hydroxide was used in alkaline region. This is in contrast to the standard electrolytic solution in which ion strength is maintained constant with buffer solution. Hence, our system is rather unusual in



**Figure 1.** Optical absorption spectra as a function of surface modification. The spectra are normalized to the plasmon peak at about 530 nm. (a) before modification, (b) surface modification without dialysis, (c) surface modification with dialysis. Note that no large absorption is apparent in the UV region after surface modification. Surface modification induced slight broadening in the surface plasmon band.

reference to the above standard system. The reason for avoiding the use of a normal buffer solution is as follows: (1) To minimize the effect of ion adsorption on the particle surface, which may disturb the surface charge; (2) to avoid inter-ion interaction in bulk solution; (3) to simplify the theoretical treatment using a simple dispersion constitution which we have mentioned already in the Introduction. Hence the objective ion species are limited to only four, H<sup>+</sup>, Na<sup>+</sup>, OH<sup>-</sup> and Cl<sup>-</sup>, and at most three of them participate in each measurement. Table 1 shows the list of ionic species used and the observed pH readings. We have derived the Debye parameter  $\kappa$  using the parameters listed in Table 1. The  $\kappa$  is given by  $(\sum z_i^2 e^2 n_i/\epsilon)$  $\epsilon_r \epsilon_0 kT$ <sup>1/2</sup>, in which  $z_i$  is the valence of *i*th ion, *e* is the elementary electric charge,  $n_i$  is the bulk concentration of *i*th ion and is connected to the total bulk ion concentration by  $n = \sum n_i$ .  $\epsilon_r$ and  $\epsilon_0$  are, respectively, the relative and vacuum dielectric constants. We used the same sample dispersion for pH measurements and for electrophoretic measurements. Since the pH reading was not stable especially for the neutral region, we had to repeat pH measurements several times with fresh sample dispersion in each case. The maximum number of measurements was 20 for pH 6.7 and the minimum was 5 for pH 3.5. We took arithmetic average for the values thus obtained as a pH value.

**Instruments.**  $\zeta$ -Potential and dynamic light scattering measurements were conducted with an Otsuka ELS 800 electrophoretic light-scattering spectrophotometer with a 10-mW He-Ne laser. Applied voltages were selected in the range 50~100 V. We washed the measurement cell at least two times with a sample dispersion to avoid unintended contamination with spurious species from the cell wall. This is because the electrophoretic behaviors are very sensitive, especially in the neutral region on account of the low ionic intensities in the sample dispersion. We also took care of the contamination from air and the wall of the vessel used so that all distilled water was used just after distillation and each measurement was finished within 2 h after commencement of the experiment to avoid the above-mentioned contamination. Electrophoretic measurements were also repeated several times because of the fluctuation of the readings. The maximum number of measurements was 14 for the neutral region and the minimum 5 for the acidic region. Size histogram was obtained with a Hitachi-8100 transmission electron microscope (TEM), operated at 200 kV with 2.1 Å point resolution. The specimen was prepared by dropping the suspension on an amorphous carbon-coated copper

pH	[H <sup>+</sup> ] (M)	[OH <sup>-</sup> ] (M)	[Cl <sup>-</sup> ] (M)	[Na <sup>+</sup> ] (M)	1/κ (nm)	ка
2.5	$3.16 \times 10^{-3}$	$3.16 \times 10^{-12}$	$5.00 \times 10^{-3}$	0		
3.5	$3.16 \times 10^{-4}$	$3.16 \times 10^{-11}$	$5.00 \times 10^{-4}$	0	15.1	0.795
4.9	$1.26 \times 10^{-5}$	$7.94 \times 10^{-10}$	$5.00 \times 10^{-5}$	0	54.4	0.221
5.8	$1.58 \times 10^{-6}$	$6.31 \times 10^{-9}$	0	0	342	0.035
6.7	$2.00 \times 10^{-7}$	$5.01 \times 10^{-8}$	0	$5.00 \times 10^{-5}$	60.7	0.198
9.4	$3.98 \times 10^{-10}$	$2.51 \times 10^{-5}$	0	$5.00 \times 10^{-4}$	18.8	0.638
11.6	$2.51 \times 10^{-12}$	$3.98 \times 10^{-3}$	0	$5.00 \times 10^{-3}$	4.54	2.643
12.7	$2.00 \times 10^{-13}$	$5.01 \times 10^{-2}$	0	$5.00 \times 10^{-2}$	1.36	8.824
13.7	$2.00 \times 10^{-14}$	$5.01 \times 10^{-1}$	0	$5.00 \times 10^{-1}$		



Figure 2. TEM photograph of surface-modified particles and the size histogram.

mesh and drying it in air. Fourier transform infrared spectra were measured with a HORIBA FT-210 infrared spectrophotometer to trace the surface modification of the particles. Ultraviolet-visible absorption spectra of the suspension were recorded on a Hitachi U-3210 spectrophotometer. No correction was made for the scattering effect.

#### Results

Characterization of Particles. FTIR, electrophoretic mobility, and high-resolution transmission electron microscopic measurements were used for the examination of surface structure of the particles. A brief summary is given for IR data.<sup>4</sup> The strong doublet at 1580 cm<sup>-1</sup> and singlet at 1404 cm<sup>-1</sup> confirmed the stretching vibration of a carboxylate group. The band at 1700 cm<sup>-1</sup> showed the carbonyl of carboxyl group. The broad peak at around 3400 cm<sup>-1</sup> identified the existence of bound water. The content of water was confirmed by thermal gravimetric analysis in the previous paper giving MSA:water  $\sim 1:1.4$ The disappearance of the band at 2548 cm<sup>-1</sup> in the RS-H region confirmed the formation of RS-Au bonding. No change was observed in the size histogram before and after the surface modification, suggesting that there was no coagulation induced by the surface modification. Figure 2 stands for the typical size histogram after surface modification and TEM photograph. The number of sample particles were 305 and the median diameter was determined to be 24 nm.

Effect of Surface Modification on Electrophoretic Behaviors. Comparison of osmotic curves was made before and after the substitution of MSA. It is not easy to determine the surfaceadsorbed species on as-prepared particles because of the contamination with byproducts through chemical reaction. After a surface modification, we confirmed that the entire surface is covered basically with one species of mercaptosuccinic acid. Figure 3 is photographs of the electro-osmotic profiles before (b) and after (a) surface modification. The monotonic peak profile as a function of cell position in (a) stands for the existence of unique species in the sample dispersion and the complex profile in (b) indicates that there are at least three different charged states in the sample particles.

Electrophoretic Mobility of Particles at Several pH. The electrophoretic mobility  $\mu$  ( $\mu$ m/s/(V/cm)) at several pH are listed



**Figure 3.** Electro-osmotic profile at several different positions from the cell wall. (a) After surface modification by MSA at pH 5.8. (b) Before modification at pH 7.0.

TABLE 2: List of Electrophoretic Mobility,  $\mu$ , Scaled Electrophoretic Mobility, Em, Surface Charge Density,  $\sigma$ ,  $\zeta$ -potential, and Surface Potential  $\psi_0$ 

pН	$\mu~(10^{-4}\mathrm{cm^2/V~s})$	-Em	$\sigma$ (C/m <sup>2</sup> )	$\zeta$ -pot (mV)	surf. pot. (mV)
3.5	-1.05	0.79	-0.1335	-19.8	-240
4.9	-2.84	2.11	-0.7590	-55.7	-397
5.8	-6.52	4.86	-1.2045	-128.0	-516
6.7	-7.15	5.34	-1.4460	-169.7	-436
9.4	-3.06	2.28	-1.5000	-61.8	-378
11.6	-2.55	1.91	-1.5000	-49.4	-305
12.7	-1.51	1.13	-1.5000	-23.9	-243

in Table 2 with relevant experimental parameters such as surface charge density  $\sigma$ ,  $\zeta$ -potential derived from  $\mu$ , and theoretical surface potential  $\psi_0$ , all of which are discussed in the Calculations section. As stated in the Experimental Section, the measured mobility scattered in a wide range especially for the neutral region, so we took a statistical average in order to determine the value. The value listed in Table 2 is thus the one after averaging process. To clarify this fluctuation, the mobility dispersion, the difference of the reading of the electrophoretic mobility at each measurement from the averaged value, is plotted in Figure 4. As seen in this figure, an increase in electrolyte



**Figure 4.** Dispersion diagram of electrophoretic mobility at several pH. Each plot is drawn for the difference from the mathematical average (horizontal line at position 0) at each pH. The plots are not symmetric against acid and alkaline end, and have maximum fluctuation around pH 7.



**Figure 5.** Optical absorption spectra as a function of pH. To avoid overlapping of spectra, the data of pH 4.9 and 11.6 are omitted in this figure. The spectra are normalized to that of the plasmon band. Three lines for pH 5.8, 11.6, and 12.7 overlapped completely. The line for pH 4.9 lies between pH 3.5 and 5.8. The plasmon peak value, 526 nm, is the same for pH 5.8, 11.6, and 12.7, but is 528 nm for pH 3.5 and 4.9.

concentration at both pH sides largely depressed the fluctuation in mobility measurement.

**Effect of pH on Absorption Spectrum.** No change was found for the peak position and line profiles for the surface plasmon band of the sample before modification as a function of pH, but a slight difference was observed for the surface-modified sample in the long wavelength region (Figure 5). This slight broadening in this region may suggests that a large change of surface charge affects the surface plasmon oscillation or more likely suggests the formation of a weakly coupled embryo in the dispersion at the acid condition.

### Calculations

Before deriving the surface potential, we need to calculate relevant parameters such as degree of electrolytic dissociation, surface charge density as a function of pH, and a maximum charge density. The external variables to take into account are the amount of MSA on the particles, pH, as well as ionic strength of the added electrolytes.

**Degree of Electrolytic Dissociation**  $\alpha$ **.** First, we abbreviate MSA bound on a particle as RH<sub>1</sub>H<sub>2</sub> since MSA is dicarboxylic acid. We assume that there is no interaction between the two carboxylic groups, so that the equilibrium constant is independent of the order of dissociation. We also assume that added electrolytes such as HCl and NaOH dissociate completely in whole pH region. Hence we have only two equilibrium constants  $K_1$  for proton H<sub>1</sub> and  $K_2$  for H<sub>2</sub> and the following four relations

hold:

1

$$RH_{1}H_{2} \rightarrow RH_{2}^{-} + H_{1}^{+} \qquad K_{1}[RH_{1}H_{2}] = [RH_{2}^{-}][H^{+}]$$

$$RH_{2}^{-} \rightarrow R^{2-} + H_{2}^{+} \qquad K_{2}[RH_{2}^{-}] = [R^{2-}][H^{+}]$$

$$RH_{1}H_{2} \rightarrow RH_{1}^{-} + H_{2}^{+} \qquad K_{2}[RH_{1}H_{2}] = [RH_{1}^{-}][H^{+}]$$

$$RH_{1}^{-} \rightarrow R^{2-} + H_{1}^{+} \qquad K_{1}[RH_{1}^{-}] = [R^{2-}][H^{+}] \qquad (1)$$

For simplicity, we abbreviate  $[H^+] = x$ ,  $[RH_1H_2] = R$ , and the initial value of *R* as  $R_0$ . Therefore the relation of mass balance and eq 1 lead to

$$R_{0} = [RH_{1}H_{2}] + [RH_{1}^{-}] + [RH_{2}^{-}] + [R^{2-}]$$
$$= R + \frac{RK_{2}}{x} + \frac{RK_{1}}{x} + \frac{RK_{1}K_{2}}{x^{2}}$$
$$= \frac{R}{x^{2}}(x + K_{1})(x + K_{2})$$
(2)

From the charge balance relation in the absence of electrolytes, we have

$$a = 2[R^{2^{-}}] + [RH_{1}^{-}] + [RH_{2}^{-}] + [OH^{-}]$$
$$= R\left(2\frac{K_{1}K_{2}}{x^{2}} + \frac{K_{2}}{x} + \frac{K_{1}}{x}\right) + \frac{K_{w}[H_{2}O]}{x}, (3)$$

in which  $K_w$  is a dissociation constant of water. From eqs 2 and 3,

$$x = \frac{R_0 x^2}{(x + K_1)(x + K_2)} \left( 2\frac{K_1 K_2}{x^2} + \frac{K_2}{x} + \frac{K_1}{x} \right) + \frac{K_w}{x}$$
(4)

Equation 4 relates the initial concentration of MSA to the observed pH of the suspension for free dissociation of MSA bound to the particle under no addition of electrolytes. This is discussed in a later section.

By definition, the degree of electrolytic dissociation is given as

$$\alpha = \frac{2[R^{2^{-}}] + [RH_{1}^{-}] + [RH_{2}^{-}]}{2R_{0}}$$
$$= \frac{2K_{1}K_{2} + (K_{1} + K_{2})x}{2(K_{1} + x)(K_{2} + x)}$$
(5)

where we neglect the term  $K_w$  that has minor contribution. Equation 5 is independent of the existence and the absence of electrolyte, because the concentration of constituent species  $[R^{2-}]$ ,  $[RH_1^{-}]$ , and  $[RH_2^{-}]$  are solely determined by eq 1. Figure 6 shows the degree of electrolytic dissociation as a function of x, in which we use the values of  $K_1$  and  $K_2$  as those of succinic acid,<sup>9</sup> because of the lack of available data for thiol derivation. Moreover, we assume no effect from gold particles on  $K_1$  and  $K_2$ . The curve shows monotonic trends as a function of pH, because the values  $K_1$  and  $K_2$  are close to each other. From this figure, the charge density of particles is easily seen as a function of pH.

**Charge Density at the Surface.** It was reported that the maximum packing density of thiol,  $S_0$ , for the gold flat surface was 0.214 nm<sup>2.10</sup> We accept this value for large particles. Since



**Figure 6.** Degree of electrolytic dissociation as a function of pH. Assuming monolayer coverage of MSA and using eq 5 with the literature values  $K_1$  and  $K_2$ ,  $\alpha$  is plotted against pH.

MSA is a divalent acid, the calculated charge density from the value,  $2e/0.214 \text{ nm}^2$ , becomes 1.5 C/m<sup>2</sup>, which is the largest ever reported among SAM particles. Compare this value to that of the fully charged metal surface in electrolytic solution,<sup>11</sup> around 0.1~0.3 C/m<sup>2</sup> and to that of sodium and potassium ion, 1.3 and 0.72 C/m<sup>2</sup>, respectively, assuming that the ionic radius the same as in a solid salt. The surface charge density as a function of pH is given by using the maximum surface charge density  $\sigma_0$  stated above and by the degree of electrolytic dissociation

$$\sigma = \sigma_0 \alpha \tag{6}$$

Several  $\sigma$  values are listed in Table 2. It should be noted that the surface of a particle is almost fully charged even at a neutral region.

MSA Coverage on a Particle. We have already reported the average MSA coverage as being 1/2 of all surface Au atoms from the elemental analysis.<sup>4</sup> This value is also confirmed by the recent STM direct observation on Au(100) and (111) surfaces.<sup>5</sup> Comparing the above data with the result of the current experiment is interesting. Assuming that there is no ionic contamination, we can estimate the average MSA coverage on the gold surface using the degree of electrolytic dissociation. The basic idea is that the number of free protons, thus pH of the solution, can be correlated to the dissociation constant of succinic acid as well as to the number of MSA molecules adsorbed on the particle, which can be calculated from the diameter of particles. The result is, hence, compared with the observed pH, 5.8, of the suspension. To calculate pH from eq 4, we need to evaluate  $R_0$ . The weight of gold in a unit volume of suspension is given by  $w = 4\pi (D/2)^3 \rho N/3$ , in which D is a diameter of particle,  $\rho$  is the density of gold, and N is the number of particles in a unit volume of suspension. The number of MSA molecules is  $N(4\pi (D/2)^2/S_0)$ . Finally, the number of MSA molecules in a unit volume is given by  $6w/\rho DS_0$ , leading to  $8.71\,\times\,10^{14}\!/\mathrm{cm^3} = 1.45\,\times\,10^{-6}\,\mathrm{M}$  using experimental values  $w = 1.39 \times 10^{-5} \text{ g/cm}^3$ ,  $\rho = 19.3 \text{ g/cm}^3$ , D = 24 nm,  $S_0 = 1000 \text{ s}^3$ 0.214 nm<sup>2</sup>. Setting  $pK_1 = 4.19$ ,  $pK_2 = 5.64$ , and  $R_0 = 1.45 \times$  $10^{-6}$  M, pH is calculated to 5.7. The above estimate is an ideal case. If half of the surface is occupied, that is, the occupied area per single MSA molecule is twice that of  $S_0$ , we have pH = 5.9.

**Derivation of**  $\zeta$ **-Potential.** It is a most common process to derive  $\zeta$ -potential from electrophoretic mobility using the

Smoluchowski or Hückel equation. However, these equations have severe restriction to the applicability in the range of  $\kappa a$ , in which  $\kappa$  is the Debye parameter and a is the particle radius. Very recently, Ohshima<sup>2</sup> derived an interpolation formula which is applicable to  $\kappa a$  in the wide range. Following this formula, electrophoretic mobility  $\mu$  is given by

$$\mu = \frac{2\epsilon_{\rm r}\epsilon_0\zeta}{3\eta} \Big[ f_1(\kappa a) - \left(\frac{ze\zeta}{kT}\right)^2 f_3(\kappa a) - \frac{m_+ + m_-}{2} \left(\frac{ze\zeta}{kT}\right)^2 f_4(\kappa a) \Big]$$
(7)

in which  $\eta$  is the viscosity of the solution,  $m_{\pm}$  are dimensionless ionic drag coefficients for cation and anion,  $f_1$ ,  $f_3$ , and  $f_4$  are a function of  $\kappa a$  and are given by

$$f_{1}(\kappa a) = 1 + \frac{1}{2[1 + 2.5/\{\kappa a(1 + 2e^{-\kappa a})\}]^{3}}$$

$$f_{3}(\kappa a) = \frac{\kappa a\{\kappa a + 1.3e^{-0.18\kappa a} + 2.5\}}{2\{\kappa a + 1.2e^{-7.4\kappa a} + 4.8\}^{3}}$$

$$f_{4}(\kappa a) = \frac{9\kappa a\{\kappa a + 5.2e^{-3.9\kappa a} + 5.6\}}{8\{\kappa a - 1.55e^{-0.32\kappa a} + 6.02\}^{3}}$$
(8)

$$m_{\pm} = \frac{2\epsilon_{\rm r}\epsilon_0 kTN_{\rm A}}{3\eta z \Lambda_{\pm}^{0}} \tag{9}$$

in which the limiting conductance of cation and anion  $\Lambda_{\pm}^{0}$  are given by the limiting mobility of constituent ions  $u_{\pm}$  as  $\Lambda_{\pm}^{0} = Fu_{\pm}^{0}$  in which *F* is the Faraday constant. From a handbook,  $u_{\pm}$  values are known for ions of H<sup>+</sup>, Na<sup>+</sup>, OH<sup>-</sup>, and Cl<sup>-</sup>, hence we can solve eq 7 using experimental  $\mu$ . Table 1 includes the list of parameters relevant to solve the above equation and the final result;  $\zeta$ -potential is given in Table 2 for the sake of comparison with surface potential.

**Surface Potential.** Surface potential is very sensitive to the adsorption of ion species to the dissociative site.<sup>12</sup> Since we have carefully selected ion species, there are only symmetric electrolyte ions as listed in Table 1. A surface potential is connected to the surface charge density as shown in the following formula for a spherical particle.<sup>13</sup>

$$\sigma = \frac{2\epsilon_{\rm r}\epsilon_0 \kappa kT}{e} \sinh\left(\frac{y}{2}\right) \left[1 + \frac{1}{\kappa a} \left(\frac{2}{\cosh^2(y/4)}\right) + \frac{1}{(\kappa a)^2} \left(\frac{8\ln[\cosh(y/4)]}{\sinh^2(y/2)}\right)\right]^{1/2} (10)$$

in which  $y = e\psi_0/kT$  and other parameters already appeared. Since all parameters in eq 10 are known, we can determine surface potential  $\psi_0$  from  $\sigma$  and it is listed in Table 2.

## Discussion

**Evidence of Self-Assembled Monolayer.** In the absence of electrolyte, the pH of the dispersion became 5.8. Assuming complete coverage, it is calculated to be 5.7 and 5.9 for half coverage. Considering the size distribution of this particle and the limited accuracy of pH-measurement at neutral region, the calculated surface density 1-0.5 layer implies that almost of all particles are fully covered by a MSA monolayer. In other words, about half of the surface gold atoms are directly bound to MSA molecules.<sup>5</sup> Recall that two gold atoms occupied 0.17 nm<sup>2</sup> on the (100) surface using a bulk lattice constant of 0.408 nm. This is consistent with other observations such as elemental



**Figure 7.** Debye length  $1/\kappa$  as a function of pH.



**Figure 8.** Diagram for  $\kappa a$  and scaled electrophoretic mobility Em. Each domain named person's abbreviation is the applicable region of the equations proposed by those authors. Concerning details, see ref 18.

analysis and STM. The uniformity of the surface is also confirmed by electro-osmosis curves after the surface modification by MSA contrast to the untreated samples, which show the existence of at least three different charged states. Observed packing density is almost the limit of coverage when taking into account the molecular size of MSA and its molecular motion.<sup>14</sup> Thus the largest surface charge density up to -1.5 C/m<sup>2</sup> is substantiated in a nanoparticle as has been mentioned in the Calculations section.

Adequacy of Equation. The well-known Smoluchowski equation correlates the electrophoretic mobility  $\mu$  with  $\zeta$ -potential at the limit of  $\kappa a \gg 1$ , while the Hückel formula is applicable to the limit of  $\kappa a \ll 1$ . In the present system, the ionic concentration ranges from  $\mu M$  to 10mM, implying that the Debye length has largely changed. We show this result clearly in Figure 7 by plotting the  $1/\kappa$  value as a function of pH where  $1/\kappa = 1.36$  nm at pH 12.7 and 342 nm at pH 5.8 at which nothing was added to the dispersion. Hence we cannot apply both equations to estimate  $\zeta$ -potential. For arbitrary values of  $\kappa a$  and  $\zeta$ , eq 7 predicts the mobility accurately. In all cases, Smoluchowski and Hückel equations gave smaller absolute values for  $\zeta$ -potential. The applicability of Smoluchowski, Hückel, Henry<sup>15</sup> as well as Ohshima-Healy-White<sup>16</sup> or O'Brien-White's numerical program<sup>17</sup> for the parameter range of  $\kappa a$  and scaled electrophoretic mobility Em is shown in Figure 8. The scaled electrophoretic mobility is a dimensionless mobility and is defined by



**Figure 9.** Comparison of  $\zeta$ -potential with surface potential  $\psi_0$  as a function of pH.

Each domain named, say, Henry, is the Em- $\kappa a$  region in which the Henry equation is good.<sup>18</sup> It should be noted that the present data points scatter into a wide range and that it is impossible to apply one of these well-known equations for the whole region. All particles deposited to sediment at the two points corresponding to pH = 2.5 and 13.7, indicating that the  $\zeta$ -potential were almost zero.

**Spectral Change.** We have noticed a slight broadening at the plasmon band by virtue of the surface modifications (Figure 1) and pH change (Figure 5). We have already pointed out two possibilities such as a surface charge directly affecting the electronic state of metallic particles or the surface charge inducing particle coagulation, although there is no direct evidence in the TEM photograph. Since we have already observed the formation of a particle crystal in the presence of hydrochloric acid added to the suspension,<sup>6</sup> the pH-dependent broadening in Figure 5 may be ascribed to the formation of flocculent in the suspension. This can be easily explained by the DLVO (Derjaguin-Landau-Verway-Overbeek) theory. On the other hand, the broadening associated with the surface modification is not yet clear.

**Comparison of Surface Potential with**  $\zeta$ **-Potential.** First we will discuss the accuracy of mobility measurement. Indeed, a large fluctuation was observed around pH 7 as shown in Figure 4. There is less quantity of additional electrolyte in this region and a small amount of contaminating ions may induce a large effect. This is the reason the fluctuation was depressed in both extreme pH regions where we added HCl or NaOH.

Figure 9 compares the observed  $\zeta$ -potential with the calculated surface potential as a function of pH. The agreement between calculated surface potential and the observed  $\zeta$ -potential is not successful, especially at both strong acid and alkaline regions. This may be due to removal of ligands from the surface of particles at such extreme conditions, which induces the overestimate of the surface charge leading to a large surface potential in the calculation. This preposition was consistent with the finding that some parts of aggregates of colloids did not disperse again when returned to neutral pH. The incompleteness of surface coverage induces strong coagulation. If the adsorption-desorption equilibrium constant of MSA as a function of pH is available, we can correct the deviation. Although there is a significant difference in quantity between theory and calculation, we have qualitative agreement between them. The difference between  $\zeta$ -potential and surface potential will be ascribed to the following reasons.

1.  $\zeta$ -Potential is defined at the slipping layer, hence its absolute value is always smaller than that of the surface potential.

2. The glass wall may contaminate the system though we washed several times with the same sample dispersions.

3. Dissolution of carbon dioxide from air though we did all experiments within a short time interval.

4. Incomplete coverage of MSA against our estimate of full coverage.

5. We used distilled water instead of ultra clean water.

Among these, 2 and 3 are an exogenous impurity effect and can be treated by "the effect of background ion". This effect largely depresses the absolute value of the surface potential.<sup>19</sup> An unknown contaminant may largely decrease the surface potential of the particles because of the low ionic intensity in the present study. The effect of the variation of ionic strength on the adsorption–desorption equilibrium has already been discussed. Reason 1 is consistent with the results shown in Figure 9 in the point that all measured potentials are less than those of theory.

We believe that the present system is a good model for charged particles in a suspension. However, it is still an open question whether the surface potential concept can be applied to nanometer-sized small particles up to 1 nm or so. Therefore the measurement of  $\zeta$ -potential for much smaller particles ranging over 2 or 3 nm in size is crucial for understanding the potential of solid surfaces in solution. We have tried to measure the  $\zeta$ -potential of the particles whose sizes are in the range from 2 to 4 nm; however, an unknown unstable scattering effect prevents the accurate determination of the mobility. It remains to us for a future task to measure the  $\zeta$ -potential of this ultimately small particle, which lies between ions with formal charge density of the order of 1 C/m<sup>2</sup> and particles with typical surface charge density of the order of 0.1 C/m<sup>2</sup>.

In conclusion, we cannot achieve completely the original objective that the measurement of  $\zeta$ -potential of a nanometersized particle will check the applicability of surface potential calculation from existing theory. We will get quantitative agreement between the two potentials in future when one solves above points from 1 to 5.

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