Tracer Diffusion of a Ligand-Stabilized Two-Shell Gold Cluster

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Diffusion coefficients have been measured for the two-shell cluster of $Au_{55}(Hdpbs)_{12}Cl_6$ (Hdpbs = diphenylphosphino-benzene-3-sulfonic acid) in water at varying ionic strengths. Hydrodynamic radius of the particles are found to be 1.44 nm as calculated from the diffusion coefficient at sufficiently high ionic strengths. This is a little larger than the radius obtained from the AFM image. The diffusion coefficients decrease with decreasing ionic strength, indicating the electrostatic drag due to the ionic atmosphere.

Metal clusters show unique properties that are different from bulk metals.[1] Ligand-stabilized clusters containing 13 (one shell),[2] 55 (two shells),[3] 309 (four shells),[4] and 561 atoms (five shells)[5] have been prepared. Efforts are being made to make two- and one-dimensional arrangements.[6] The size of metal cores can be obtained from the transmission electron microscopy (TEM) image. In view of the use as catalysts and as advanced materials in electronics, it is important to investigate thickness and structure of the protective agent. Total size of clusters with protecting agents have been obtained only recently from atomic force microscopy (AFM)[6] and scanning tunneling microscopy (STM)[7] images. By comparing hydrodynamic radii obtained from diffusion measurements and radii obtained from TEM image, we have recently investigated the arrangement of protecting agents around metal clusters.[8,9] This method has an advantage of measuring the size in solution. We report here the application of this method to well-defined two-shell clusters of gold. Because the size of the cluster is one of the smallest in colloidal particles, it is of great interest to investigate the effect of ionic atmosphere on the tracer diffusion of the particles and to compare it with those on larger colloidal particles such as micelles,[10,11] polystyrene latex spheres,[12-14] and gold sols.[14]

$Au_{55}(Hdpbs)_{12}Cl_6$ (Hdpbs = diphenylphosphino-benzene-3-sulfonic acid) was prepared at Universität Essen.[3f,6] For diffusion measurements, Nadpbs was purchased from Tokyo Kasei, and Hdpbs and Bu_4Ndpbs were obtained by ion exchange of Nadpbs. Diffusion coefficients were determined by the Taylor dispersion method.[15] In this method, a small amount of solution is injected into a solvent flowing through a capillary tube. As a results of convection and molecular diffusion, the solute is dispersed along the tube. In this study, a solution of 20 mm^3 was injected into a solvent flowing through a teflon tube of 1 mm i.d., 20 m in length, and coiled in a 35 cm circle. The solvent contained Hdpbs + HCl, Nadpbs + NaCl, or Bu_4Ndpbs + Bu_4NBr, and the solution contained 6×10^{-5} M (1 M = 1 mol dm^{-3}) $Au_{55}(Hdpbs)_{12}Cl_6$ and Hdpbs + HCl, Nadpbs + NaCl, or Bu_4Ndpbs + Bu_4NBr of the same concentration as the solvent. Concentration profiles of the clusters at the end of the tube were detected by the absorption at 450 nm using a spectrophotometric detector for HPLC (Waters, model-490). Other details have been stated elsewhere.[10]

Table 1. Diffusion coefficients for Au_{55} clusters in aqueous solutions of diphenylphosphinobenzenesulfonate at 298.2 K

$[dpbs^-]$ / mM	[salt] / mM	D / 10^{-10} m^2s^{-1}	r_s / nm
	Hdpbs + HCl		
0.1	0	1.49 ± 0.03	1.65
0.5	0	1.53 ± 0.03	1.61
1	0	1.60 ± 0.02	1.50
1	9	1.69 ± 0.13	1.45
	Nadpbs + NaCl		
0.1	0	1.38 ± 0.01	1.77
1	0	1.45 ± 0.01	1.69
1	9	1.59 ± 0.01	1.55
1	39	1.66 ± 0.04	1.48
1	99	1.70 ± 0.02	1.44
	Bu_4Ndpbs + Bu_4NBr		
0.5	0	1.26 ± 0.04	1.94
1	0	1.28 ± 0.04	1.92
1	9	1.59 ± 0.02	1.54

Diffusion coefficients obtained are listed in Table 1. These are average values of four or more determinations. Also shown are Stokes radii calculated from

$$D = k_BT/f \qquad (1)$$

by setting $f = 6\pi\eta r_S$, where k_B is the Boltzmann constant and η is the viscosity of the solvent. Diffusion coefficient decreases with decreasing ionic strength. At the same ionic strength, they increase in the order in Bu_4Ndpbs < Nadpbs < Hdpbs solutions. This suggests that the decrease is due to the electrostatic drag by counter ions. With increasing ionic strength, diffusion coefficients increase and reach a constant value irrespective of the counter ions ($D = 1.70 \times 10^{-10}$ m^2 s^{-1}).[16] Here the effect of ionic atmosphere is small and the Stokes radius (r_S = 1.44 nm) reflects the solute size. From the AFM image of the monolayers of the same clusters, the radius of the clusters including the protecting ligand has been obtained to be 1.2 ± 0.1 nm.[6] Note that the radius obtained here is 0.2 ± 0.1 nm larger than that of the dried monolayer.

In Figure 1, diffusion coefficients are plotted as a function of κa, which is the ratio of the cluster radius (a = 1.44 nm) to the Debye screening length κ^{-1}. κ is defined as

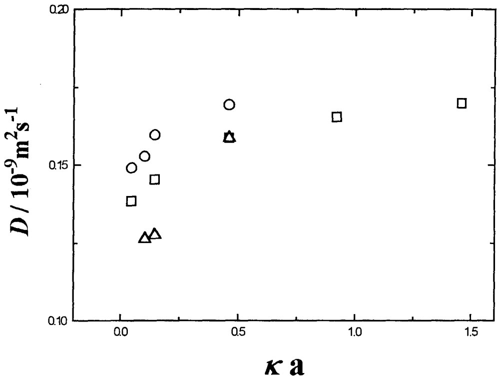

Figure 1. Diffusion coefficients of the Au_{55} clusters in aqueous solutions of Hdpbs + HCl (○), Nadbps + NaCl (□), and Bu_4Ndbps + Bu_4NBr (△) as a function of κa.

$$\kappa^2 = e^2 \sum_i n_i z_i^2 / (\varepsilon_0 \varepsilon_r k_B T) \qquad (2)$$

where e is the electronic charge, n_i is the concentration of the i th ion, z_i is the valency of the i th ion, ε_0 is the vacuum permittivity and ε_r is the relative permittivity of the medium. When the κa value is smaller than 0.5, diffusion coefficients decrease with decreasing κa. For ionic micelles,[10,11] the decreases are observed when the κa value is smaller than 1, and for polystyrene latex spheres[12-14] and gold,[14] the decreases start at higher κa values. These results show that the drag force by ionic atmosphere becomes appreciable at smaller κa for smaller particles.

When the κa value is smaller than 1, there are theoretical predictions for D values to increase with decreasing κa.[17] Schmacher and van de Ven[14] found that the diffusion coefficients of both gold particles (ca. 20 nm diameter) and latex spheres (ca. 40 nm diameter) increase with decreasing κa, i.e., D values show minima at κa = 1. However, Okubo[12] found that D values of latex spheres of 120 nm decrease with decreasing κa until the latter value reaches 0.2. Gorti[13] et al. also found D values of 18 nm diameter latex spheres to decrease with decreasing κa value down to 0.6. For ionic micelles, we have found that D values decrease with decreasing κa values down to 0.3. In this study, using one of the smallest colloidal particles, we have achieved the lowest κa value (κa = 0.05). D values are found to keep decreasing with decreasing κa until the latter reaches 0.05. This means that when the radius of the ionic atmosphere is 20 times larger than the particle radius, the drag due to the ionic atmosphere is still acting.

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