≪연구논문≫ The Journal of Optical Society of Korea(Korean Edition) Volume 3, Number 3, September 1992

Light Scattering from Restructured Colloidal Silica Aggregates

Young-Hoon Rim*

Department of Physics, Yonsei University, Wonju, Kangwon 222-701, Korea

(Received: August 27, 1992)

We present the static and dynamic light scattering results of the salt induced restructured colloidal silica aggregates. We also report the results from the transmission electron micrographs which confirms the individual sizes of the particles and the local structure of the ramified aggregates. The fractal dimensions of the restructuring silica aggregates are considerably different with in-situ light scattering measurements. The measured fractal dimensions, D_f, is 2.21 for the 0.5 wt.% concentration of the salt induced Ludox-AM. The Rayleigh linewidth for 0.1 wt.% concentration of Ludox-AM is discussed.

In the study of materials with random structures, the understanding is essential for the process of aggregation or the flocculation of small particles to form larger clusters and structures. The results of the process of aggregation or the flocculation are important technologically and scientifically. Dynamic or quasielastic light scattering (QELS) technique is an essential tool in unveiling the kinetics of the aggregation process and in study of the particle sizes of the distribution in colloidal aggregates.[1,2] It measures the time dependence of the intensity fluctuation through the autocorrelation function of the scattered light. The static light scattering provides the informative fractal structure of the aggregates on scattering from the clusters. In case of the static light scattering, it measures the angle dependence of the time averaged intensity fluctuation of the scattered light. Recently, the aggregation behavior of colloidal gold and silica has been studied extensively as a model system of the fractal geometry of the aggregates.[3-8] These two classes of aggregation, both assumed to be irreversible, are characterized in terms of the diffusion-limited aggregation (DLA or Witten-Sander model; $D_f=2.5$), diffusion-limited cluster-cluster aggregation (DLCA or CA; $D_f=1.75$), reaction-limited cluster-cluster aggregation (RLCA; $D_f=2.05$).[3-10]

From the visual observations, the salt induced silica particle aggregation for the in-situ measurements may be in progress the following way; first, small spherical negative-surface-charged particles are screened from the diffusive salt solution and become neutralized particles individually, second, each neutralized particle is acting like a spherical dipole which attracts one another due to the van der Waals force and then forms a spherical shape of aggregates of the particles. The typical size of the aggregates is a few mm approximately. The aggregates of particles, however, are very much fragile against the external disturbance which easily makes them to be sediment and agglomeration. It is, therfore, interesting to testify whether the restructured aggregates have the same fractal dimensions as the definite in-situ light scattering measurements of aggregation.

In case of the static light scattering, if the size of cluster is much larger than the incident wavelength, then the scattered intensity is expressed by[10]

$$I \propto q^{-D_f}, \tag{1}$$

where D_f is the fractal dimension and q is the wave vector defined by

$$q = \frac{4\pi n}{\lambda} \sin(\theta/2) \tag{2}$$

Here, n is the solvent refractive index, λ the incident wavelength, and θ the scattering angle.

For the dynamic light scattering, if the particle dispersion is sufficiently dilute, then the average of polar-

ized intensity autocorrelation function in terms of a Laplace transform can be expressed by[12]

$$\langle I_{VV}(0)I_{VV}(t)\rangle - A = B'\left(\int_0^\infty \exp[-\Gamma t]\ G(\Gamma)\,d\Gamma\right)^2, \tag{3}$$

where $\Gamma \equiv q^2D$ and the normalized decay constant distributon $G(\Gamma)$ is defined by

$$G(\Gamma) = \frac{dR}{d\Gamma}\,\alpha^2(R)\ P(R)\ f(R). \tag{4}$$

The Γ is the Rayleigh linewidth or the mean decay rate, A and B' the constants, R the radius of the gyration, D the particle translational diffusion coefficient, $\alpha(R)$ the polarizability, $P(R)$ the form factor, and $f(R)$ the distribution function. For spherical particles, the quantity $dR/d\Gamma$ may be evaluated easily from the hydrodynamic Stokes-Einstein relationship,[11,12]

$$D = \frac{k_B T}{6\pi\eta R}, \tag{5}$$

where k_B is Boltzmann's constant, T the absolute temperature, and η the solvent viscosity.

Scattering samples were made from commercial colloidal silica (Ludox-AM) in the following way : Ludox-AM was diluted to 1.0% (pH=9.0) and 0.2% (pH=7.7) by weight and added the same amount by volume of the salt solution of 2 M concentration at the pH level of 4.0. The final concentrations of these samples were 0.5 wt.% and 0.1 wt.% at 1 M NaCl, approximately. The pH level of these samples was reduced to 6.0 and 4.4, respectively. For the light scattering measurements, the samples were aged for a couple of months at the room temperature. After aging, the samples were agitated by using the ultrasonic vibrator before performing the light scattering experiments. From the static light scattering measurements, we obtained the fractal dimensions $D_f = 2.21$ for the 0.5 wt.% Ludox-AM sample at 1 M NaCl and $D_f = 1.52$ for the 0.1 wt.% silica sample at 1 M NaCl. This is quite surprising result unlikely to the one from the in-situ light scattering measurements,[4,6] especially, for the lower concentration of the Ludox-AM sample. Schaefer et al. reported the fractal dimension $D_f = 2.12 \pm 0.05$ from in-situ measurements with two concentrations (0.1 wt.% at 1 M NaCl, 0.5 wt.% at 1 M NaCl) of salt induced silica monomers of Ludox SM particles.[4] Martin et al. found $D_f = 1.84 \pm 0.08$ from the light scattering measurements on vapor-phase aggregates of silica.[6] The scattering exponent was 2.05 ± 0.06 in the slow aggregation of colloidal silica [7] and 1.73 ± 0.06 in the fast aggregation of colloidal silica.[4] Rim et al. found similar results to the one in the slow aggregation of colloidal silica.[4]

Fig. 1 shows the results from the static light scattering measurements for two different concentrations of the salt induced samples of Ludox-AM. The intensity was proportionally increased to the concentrations of the samples. This is manifest since the size of clusters may depend on the concentrations. The salt induced samples showed the fractal geometry, while no salt induced sample showed the nonfractal gemetry.

Transmission electron microscope (TEM) micrographs showed not only the individual particle size and local structures of the aggregates but also the size of the clusters. TEM samples were provided by evaporating the liquid from the 200 meshed copper grid. Three

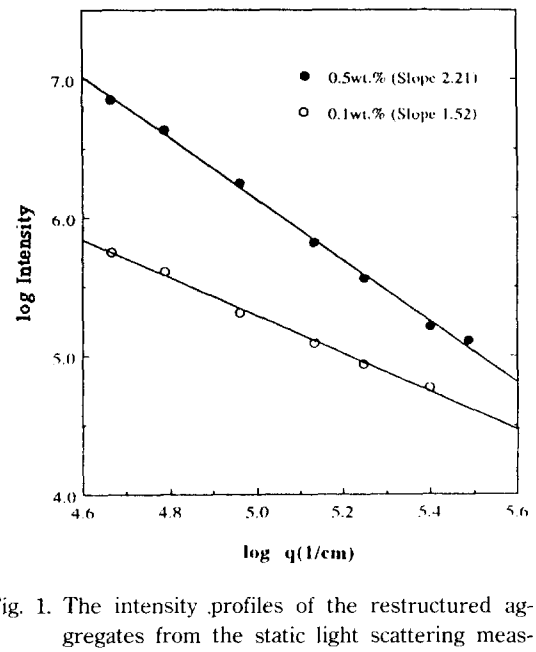

Fig. 1. The intensity profiles of the restructured aggregates from the static light scattering measurements for two different concentrations of the salt induced samples of Ludox-AM.

types of Ludox were used : AM, AS and CL. These three materials are all nominally silica but they have qualitatively different surface chemistry. Ludox-AS is essentially pure silica. Thus, it has a negative surface charge at pH level above two and the magnitude of the surface charge dependent on the level of pH. Ludox-AM had aluminum substituted into the tetrahedral sites which created a fixed negative charge. This material was, therefore, always negative and the magnitude of the charge was insensitive to change in the level of pH concentrtions. Ludox-CL had a thin coated alumina on each particle and carried a positive charge at pH values below eight. TEM measurements for these samples showed that they were very spherical and closely sized (AM was nominally 12 nm in diameter, AS was 22 nm, and CL was 12 nm). Samples were examined by both TEM selected ared diffraction pattern (SADP) and X-ray diffraction. These examinations confirmed that the structures of samples were amorphous. Here, we note that the agglomerations are the three-dimensional process in the solution, while the TEM shows the two-dimensional structures at the nearly flat edge on the areas of local structure examinations. A typical picture of a part of the aggregate was shown in Fig. 2.

The Brookhaven Instrument Corporation (BIC) laser light scattering system was used for the dynamic and static light scattering measurements. For static light scattering, we were able to measure the intensities

Fig. 2. Transmission electron micrograph of a silica (Ludox-AS) cluster.

from 10° to 160°. For high angle measurements more than 105°, some backscattering effects were observed for the static light scattering intensities. A vertically polarized Ar laser beam ($\lambda=5145$Å) was used as the incident light source. The autocorrelator of the BIC system provided the average particle size at the moment of the dynamic light scattering measurements and the distributions of the scattered intensities from the polydispersed clusters. To find out the proper distribution functions, the various numerical techniques were approached such as cumulant analysis, a double exponential, exponential sampling analysis, non-negative constrained least squares, and Contin. The exponential sampling analysis is known as Pike-Ostrowski analysis and Contin[13] is a large program being applied to a quasi-continuous Laplace inversion on the normalized autocorrelation function using nonnegativity to preclude nonphysical results. A feasibility study on Contin is performed for the analysis of the autocorrelation function on the characterization of phospholipid bilayer vesicles.[14]

The average size of the restructured clusters, which was measured at 90°, were several microns and 80 nm approximately for the 0.5 wt.% and the 0.1 wt.% Ludox-AM at 1 M NaCl, respectively. This represents that the scattered fields for the 0.5 wt.% silica lie in the regime of $qR\gg1$ but the fields for the 0.1 wt.% silica lie in the different limit of the Rayleigh regime $qR\ll1$. For the salt induced sample with the concentration of 0.1 wt.% the dynamic light scattering measurements showed that the intensity distribution from the cluster of particles was sensitive at low angle scattering. In other words, at the low angle the scattered intensity from the large cluster of particles was dominant. The Rayleigh linewidth data for the salt induced silica with 0.1 wt.% concentration were shown in Fig. 3, and excel lent p ower-law behavior was found in the experimental range of 45 nm$<1/q<$350 nm. These Rayleigh linewidth data were obtained by the second order cumulant method and lied with 99.8% statistical confidence. From the slope of these data for the sample of 0.1 wt.% concentration, we found the Rayleigh linewidth $\Gamma\sim q^{2.36}$ from the best curve fit in the regime of $qR<1$. Correspondingly the translational diffusion coefficient was

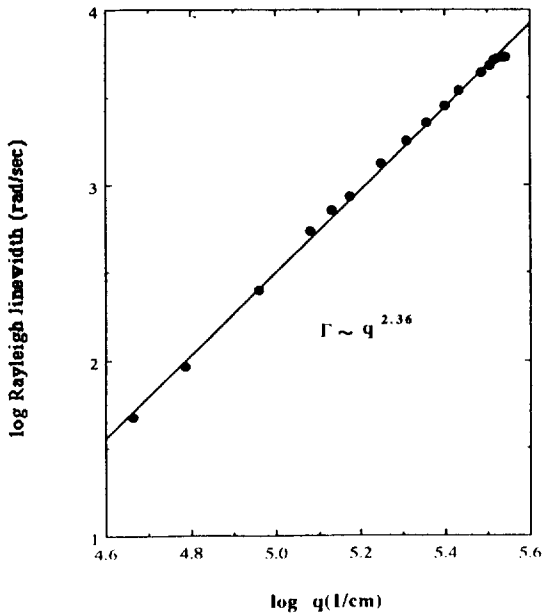

Fig. 3. The Rayleigh linewidth data for the salt induced silica (Ludox-AM) with 0.1 wt.% concentration.

proportional to the power of 0.36 of the momentum transfer, i.e., $D \sim q^{0.36}$. This result could be used to calculate the corresponding radius of the gyration R from the Eq. (5), especially, for the spherical clusters. The estimated effective Rayleigh diameter from the second cumulants analysis at 90° was 80.1 nm. The particle size estimation was a little different for the different analyses of the spectrum, however, the estimation of the average effective diameter of the cluster was consistent at the high momentum transfer regime. In terms of the power-law and the limit of regime, this result is very inconsistent with the previous in-situ measurements for colloidal silica and vapor-phase aggregates of silica.[5,15] This may be the results from the nonfractal structure since the average size of the aggregates was considerably small.

The restructured aggregates of the 0.5 wt.% colloidal Ludox-AM had a quite high value of the fractal dimension compared to the one for the in-situ light scattering measurements. It may be understood as the result of the sedimentation as follows : the average size of the restructured aggregates is much smaller than the one from the in-situ measurements and, consequently, the sediments of the restructured silica aggregates are being more closely packed and increased the number density of the scattering particles. These highly dense aggregates cause the immense multiple scattering for the scattered light. It may also be possible for these restructured silica aggregates to have highly anisotropic agglomerations through the restructuring processes of the aggregates. The dynamic light scattering experiment is not adequated for the size determinations for the large clusters or aggregates with a high concentration, since the multiple scattering effect is very strong among those aggregates and consequently the autocorrelator can not separate the second signals from the cluster-cluster interaction due to the large size of the aggregates. For the more diluted 0.1 wt.% silica sample, however, the multiple scattering process was negligible since there was no observable sedimentation at the scattering regions and the average size of the aggregates was considerably small. These may be the reasons why the fractal dimension was very different with high concentration case.

In summary, we have shown that the static and dynamic light scattering results from the restructured colloidal silica aggregates. From the static light scattering measurements, we obtained the fractal dimensions $D_f = 2.21$ and $D_f = 1.52$ for the 0.5 wt.% and the 0.1 wt.% Ludox-AM sample at 1 M NaCl, respectively. These were quite surprising results unlikely to the one from the in-situ light scattering measurements. For the high concentration sample, the high value of the fractal dimension may be understood as the results of the multiple scattering of the light and the anisotropic agglomerations through the restructuring processes of the aggregates. For the sample of 0.1 wt.% concentration, we found the Rayleigh linewidth $\Gamma \sim q^{2.36}$, experimentally, in the regime of $qR < 1$. The static and dynamic scattering results from lower concentration may be explained by the nonfractal structure because the average size of the aggregates were considerably small.

ACKNOWLEDGEMENTS

Y. H. R. would like to acknowledge support from

the Korean Science Foundation (KSF) Grant for '92 domestic Post-Doc.

REFERENCES

[1] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).

[2] B. E. Dahneke, *Measurement of Suspended Particles by Quasi--Elastic light Scattering* (Wiley, New York, 1983).

[3] D. A. Weitz and M. Oliveria, Phys. Rev. Lett. **52**, 1433 (1984).

[4] D. W. Schaefer, J. E. Martin, P. Witzius and D. S. Cannell, Phys. Rev. Lett. **52**, 2371 (1984); J. E. Martin, J. P Wilcoxon, D. W. Schaefer and J. Odinek, Phys. Rev. A. **41**, 4379 (1990); Y. H. Rim, J. D. Cawley, R. R. Ansari and W. V. Meyer, *Ceramic Transactions Forming Science and Technology for Ceramics* **26**, 54 (1991).

[5] J. E. Martin and D. W. Schaefer, Phys. Rev. Lett. **53**, 2457 (1984).

[6] C. Aubert and D. S. Cannell, Phys. Rev. Lett. **56**, 738 (1986).

[7] J. E. Martin, Phys. Rev. A. **36**, 3415 (1987).

[8] H. M. Lindsay, M. Y. Lin, D. A. Weitz, P. Sheng, Z. Chen, R. Klein and P. Meakin, Faraday Discuss. Chem. Soc. **83**, 153 (1987).

[9] P. Meakin, Ann. Rev. Phys. Chem. **39**, 237 (1988).

[10] R. Jullien and R. Botet, *Aggregation and Fractal Aggregates*, (World Scientific, Singapore, 1987).

[11] B. Chu, *Laser Light Scattering*, Ch. 11, Academic Press, New York (1974).

[12] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, Ch. 6, Pergamon Press, Oxford (1989).

[13] S. W. Provencher, J. Hendrix, L. De Maeyer and N. Paulussen, *J. Chem. Phys.* **69**, 4273 (1978).

[14] E. Stelzer, H. Ruf and E. Grell, "Analysis and Resolution of Polydisperse Systems", in : *Photon Correlation Techniques in Fluid Mechanics*, ed. E. O. Schulz-DuBois (Springer-Verlag, Berlin Heidelberg, 1983).

[15] J. E. Martin, D. W. Schaefer and A. J. Hurd, Phys. Rev. A **33**, 3540 (1986).

재구조화된 콜로이드 실리카 응집체에 대한 광 산란

임 영 훈
연세대학교 물리학과

(1992년 8월 27일 받음)

소금물에 유도된 콜로이드 실리카 응집체의 재구조에 대한 정적 및 유동 광산란 결과를 나타냈다. 또한 투과전자현미경을 이용한 사진결과로부터 입자들 각각의 크기 및 그물 모양으로 갈라진 응집체에 관한 미세구조를 확인하였다. 재구조화된 실리카 응집체에 대한 프랙탈 차원들은 현상태 광산란 측정결과들과 상당히 달랐다. 소금물에 유도된 0.5 wt.% 농도의 Ludox-AM에 대한 프랙탈 차원 D_f는 2.21로 측정되었다. 0.1 wt.% 농도의 Ludox-AM에 대한 Rayleigh 선폭을 논의한다.