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SMALL ANGLE NEUTRON SCATTERING STUDY OF SILICA SUSPENSIONS

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ABSTRACT

Two types of silica were used: one is Aerosil-130 silica, which is easily aggregated in water and the other is Snowtex-C dispersed in water. These silicas were mixed with an aqueous solution of hydroxypropyl methyl cellulose (HPMC) that adsorbs on the silica surfaces to make silica suspensions. Small angle neutron scattering (SANS) technique was used to understand the structures and interactions of the silica suspensions and the corresponding silica slurries (no HPMC) as functions of HPMC and silica content. The wave vector q was ranged 0.03 to 0.8 nm^{-1}. In the scattering curves for Aerosil silica slurries and suspensions below $q = 0.1 nm^{-1}$, a power-law exponent of 2.1 was obtained independent of silica content. The scattering curves at higher q, however, approached a power-law scattering with an exponent of -4, namely followed the Porod's law. It was found that adsorption of HPMC did not effect on the scattering curves. On the other hand, for Snowtex-C the peak was observed at the intermediate q in the scattering curves, whose position shifts to higher q with an increase in silica content, indicating that an average distance between silica particles decreases. Snowtex-C suspensions showed an increase in scattering intensity below $q = 0.1 nm^{-1}$ by adsorption of HPMC.

INTRODUCTION

Understanding of the structures and interactions in colloidal dispersions has recently advanced due to the application of small angle neutron scattering (SANS).[1] In SANS measurements many different types of colloidal system have been used, such as the dispersions of latex particles,[2] oxide sols,[3-5] and clay.[6] Among the oxide sols silica particles were often adapted since their characteristics were relatively known. Aggregation behavior of the silica particles dispersed in

water strongly depend on pH.[7] At pH = 2 the silica particles carry zero charge on the surface and below pH = 2 the silica particles become positively charged and meta-stable. On the other hand, above pH=2 the silica particles own negative charge and they tend to aggregate with an increase in pH. In the range pH 8-10 repulsion forces lead to stable silica dispersions and the silica particles dissolve in water beyond pH = 11.

In this study, we investigated the structural changes in the silica particles dispersed in water and in aqueous solution of polymer chains that adsorb on the surfaces of the silica particles in terms of the distances between the silica particles obtained from the SANS measurements.

EXPERIMENTAL

Materials We used two silicas. Aerosil-130 supplied from Aerosil Japan (Yokkaichi) was fumed silica. From the manufacture, the surface area is 141 m^2/g and the particle diameter is 16 nm. It was dried in a vacuum oven at 200°C.[8] Snowtex-C dispersed in water, which is a typical colloidal silica due to repulsion forces between negative charges on silica surfaces was supplied from Nissan Chemical Co. and its diameter is ranged 10 to 20 nm. It was used without further purification.

HPMC sample of 65SH-400 supplied from Shin-Etu Chemical Co. was purified by precipitation of its aqueous solutions containing 0.02% NaN_3 into acetone and freeze-dried from its aqueous solution. The molecular weight of HPMC was determined from the intrinsic viscosity measurements in aqueous 0.1 N NaCl solution at 25 ± 0.05°C using an Ubbelohde viscometer.[9] The molecular characteristics were as follows: the molecular weight (Mw) of HPMC is 403 x 10^3, the degree of substitution (DS) of OCH_3 group is 1.8, and the molar substitution (MS) of OC_3H_7OH group is 0.15.

Water purified by a Millipore Q-TM system was used. Pure grade quality NaN_3 was used as a preservative for HPMC.

Silica slurry of Aerosil-130 was prepared by dispersing the silica powder in water by mechanically shaking and ultrasonic irradiation and the resulting silica slurry was turbid. An aqueous solution of HPMC with known concentration was added to the resulting silica slurry and the mixture, hereafter called as the silica suspension was mixed well by mechanically shaking and by further ultrasonic irradiation to obtain a homogeneous mixture.

On the other hand, Snowtex-C dispersion was mixed with an aqueous HPMC solution to prepare a desired mixture by mechanically shaking. Silica content was ranged 2.5 to 10 wt. % and HPMC concentration was fixed 1.5 wt. % for the respective silica content.

SANS Instrument SANS experiments were performed using the JAERI 20 m SANS instrument. The wavelength λ was selected to be 0.625 nm by using a velocity slector with variable speed and pitch and the wavelength resolution is $\Delta\lambda/\lambda$ = 15%. The monochromatic beam was collimated by a series of circular apertures of diameter 10 mm. The 5 mm circular aperture was suited before the sample cell to define the sample illuminated. The samples were transferred to quartz cells of path length 1 mm. The scattered neutrons were detected by a ^3He area detector of 58 cm diameter circle containing 128 pixel elements. The sample to detector distances were 3 and 10 m, corresponding to the wave vector q range 0.03 to 0.8 nm^{-1}. The measuring temperature was 25 ± 1°C. Data were corrected

for empty cell background. Data taken at 3 m sample to detector distance cover the q range 0.09 to 0.8 nm^{-1} and data at 10 m range from 0.03 to 0.25 nm^{-1}.

RESULTS AND DISCUSSION

Adsorption study of HPMC on silica surfaces was reported in a previous paper.[10] The adsorption isotherm was a rounded-shape isotherm because of the polydispersity of HPMC sample. The adsorbed amount of HPMC at the plateau region was 0.1 g/g. As a concentration of HPMC studied here was well in the plateau region of the adsorption isotherm of HPMC, silica particles were saturated with HPMC chains and free HPMC chains were remained in water.

Aerosil Silica-130 As mentioned above, the appearance of turbidity in the silica slurry shows aggregation of silica particles in water. Figure 1 shows the scattering intensity I(q) as a function of q for two silica slurries of 2.5 and 7.5% silica content. The intensity at low q range decreases with an exponent of -2.1, namely corresponding to the fractal dimension and at high q region I(q) tends toward the Porod's law, irrespective of the silica content. Similar scattering curves were obtained the silica slurries of 5.0 and 10 %. This indicates that the silica slurry is a kind of fractal object and its structure is self-similarity. However, the resulting fractal dimension does not agree with the two most popular models,[11] diffusion-limited aggregation and diffusion-limited cluster-cluster aggregation. Similar fractal dimension was obtained for the colloidal aggregates of silica particles by addition of salt.[12] The exponent of -4 at high q range can be interpreted by scattering from the individual silica particles making up the aggregates. Therefor, from the q value at which the crossover occurs between the two exponents, we can calculate nominal radius of gyration of silica particle, 5.8nm.

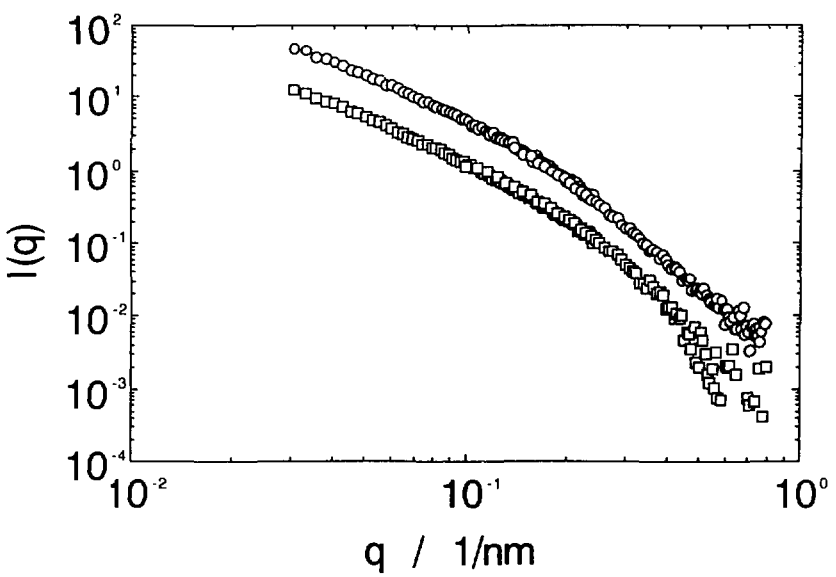

Figure 1. Double logarithmic plots of scattering intensity I(q) against q for the Aerosil-130 silica slurries : (□) 2.5% silica content; (○) 7.5% silica content.

In Figure 2, the scattering curves of the 2.5 and 7.7% silica suspensions are displayed. They are superimposed to those of the corresponding silica slurries without any correction This means that the addition of HPMC to the silica slurries does not induce any changes in the aggregated structures of silica particles dispersed in water, although adsorption of HPMC on the silica particles occurs.

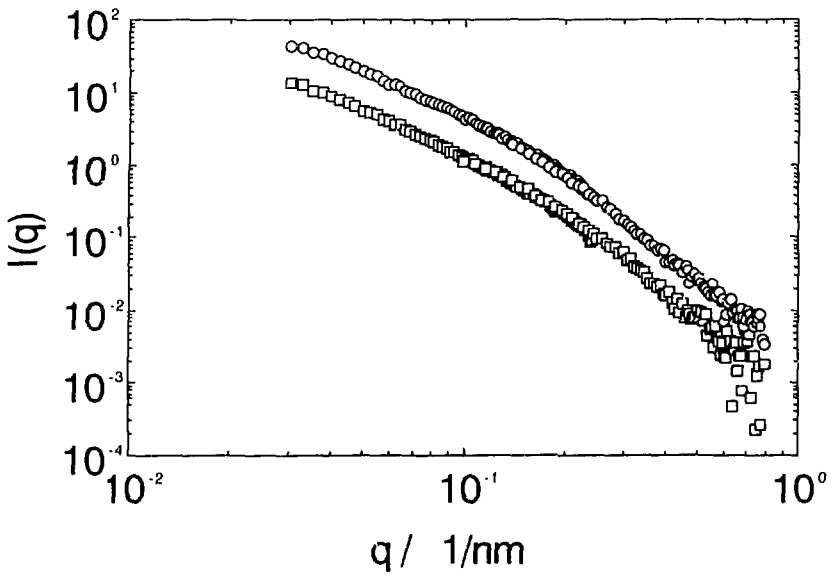

Figure 2. Double logarithmic plots of scattering intensity I(q) against q for the Aerosil-130 silica suspensions. Symbols are the same as in Figure 1.

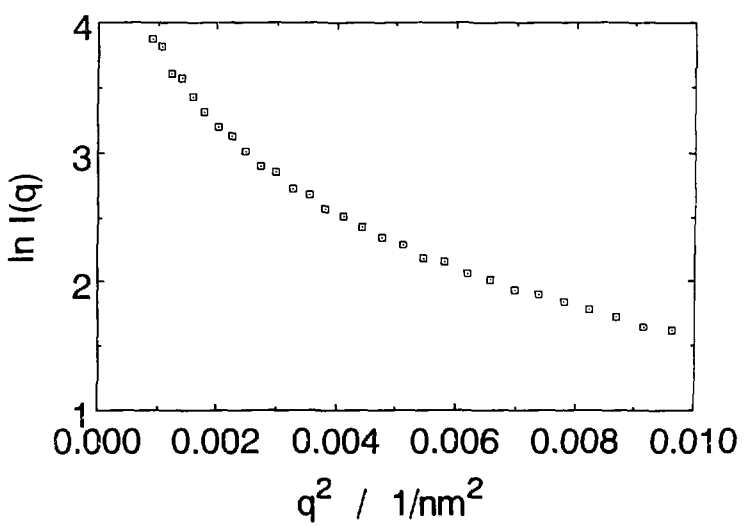

Figure 3. A Guinier plot of Aerosil-130 silica suspension of 7.5% silica content.

To deduce the average size of the particles dispersed in medium, the Guinier approximation is sometimes used for uniform particles of any shape. A typical Guinier plot of the 7.5% silica slurries is represented in Figure 3. It clearly indicates that there is no distinctive linear behavior. This suggests that either the particles are too polydisperse in size or that the Guinier region is not covered in the experiment. In either case, no structural information can be extracted from the Guinier plot as far as our data are concerned. Since a detailed structural analysis taken into account polydispersity is needed, such an analysis is under proceeding and some results will be appeared in the future.

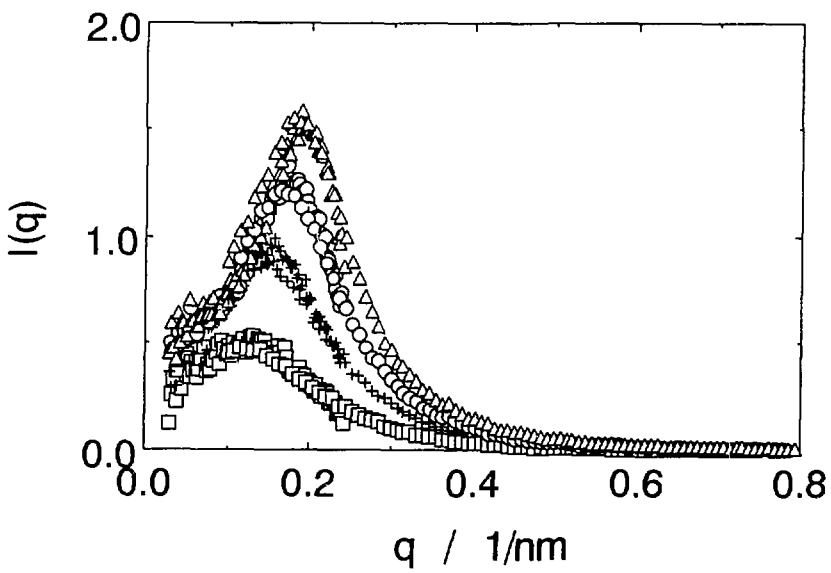

Figure 4. Scattering intensity I(q) as a function of q for various Snowtex-C dispersions: (□) 2.5% silica content; (+) 5.0% silica content; (○) 7.5% silica content; (△) 10% silica content.

Snowtex-C Figure 4 shows the scattering curves of Snowtex-C dispersions of 2.5, 5.0, 7.5 and 10 % silica content. In the respective scattering curves a peak was observed. The peak shifts to high q systematically with the silica content: the more silica content, the shorter the distance of separation between neighboring spheres. The separation distances calculated from the Bragg's relation, $D = 2\pi/q$ are 48.3, 40.5, 36.9, and 33.8 nm for the colloidal silica dispersions of 2.5, 5.0, 7.5 and 10 % silica content, respectively. These separation distances are compared with the average distance (d) calculated from the relation $d = (4\pi\rho/3C)^{1/3}$ based on a simple model, where ρ is the density of silica (2.2 g/cm^3) and C is the silica concentration in the dispersion. Such average distances are 57.4, 45.5, 39.8, and 36.1 nm for the corresponding silica dispersions. Their values are in good agreement with those obtained from the SANS measurements.

In Figure 5 the scattering curves of colloidal silica dispersions of 2.5, 5.0, 7.5, and 10 % silica content in aqueous HPMC solution are displayed as a function of q. A comparison of the scattering curves in Figures 4 and 5 shows that broadening in

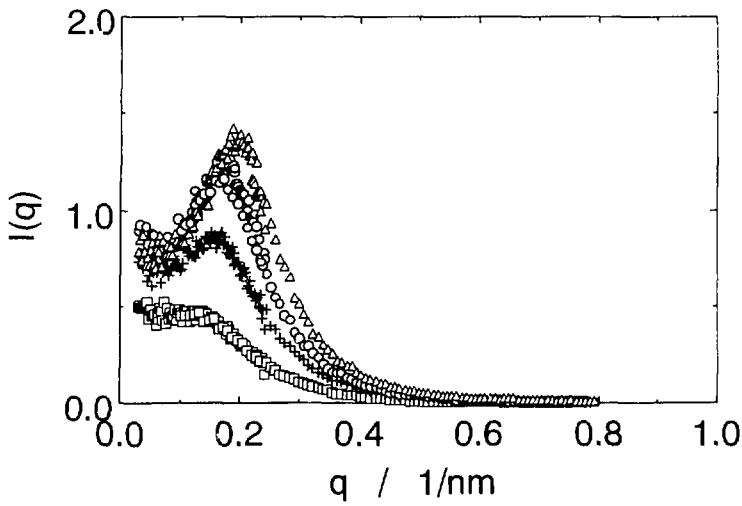

Figure 5 Scattering intensity I(q) as a function of q for various Snowtex-C dispersions in aqueous HPMC solution. Symbols are the same as in Figure 4.

the peak occurs and the scattering intensity at lower q range increases by adsorption of HPMC. This means that the short-range order resembling a crystal becomes loosing by screening the electrostatic repulsions forces between the silica particles, leading to formation of the large size aggregates in the dispersions.

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