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Analysis of a Polydisperse System Using Small-Angle X-Ray Scattering*

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The small-angle X-ray data from a polydisperse solution of sodium silicate have been measured in the concentration range 3.6-169 mg/cm^3 using a *Kratky* camera. The following values of the particle parameters were obtained: the average radius of gyration = 7.5 nm, the average particle weight = 900 000, the average volume = 671 nm^3, and the average particle surface area = 717 nm^2.

From the above parameters and the apparent specific volume, analysed to be 0.422 cm^3/g, the water content of the silicate particles was determined to be 3% (by weight).

From small-angle X-ray measurements, performed on solutions exposed to a hydrodynamic field, it is indicated that at least the larger particles in the solution have a relatively symmetric shape. Based on this observation it was assumed that the particles in solution are spherical, and particle size distribution functions were calculated using a least-squares program. It was found that the distribution cannot be described by a simple function, such as a *Gauss*ian function; instead, the distribution follows a histogram with three local maxima.

(Keywords: Distribution functions; Flow orientation; Polydisperse system; Least-squares analysis; Small-angle X-ray scattering; Sodium silicate)

Analyse eines polydispersen Systems mittels Röntgen-Kleinwinkelstreuung

Eine polydisperse Lösung von Natriumsilikat wurde im Konzentrationsbereich 3,6—169 mg/cm^3 mittels einer *Kratky*-Kamera untersucht. Folgende Partikel-Parameter wurden ermittelt: Mittlerer Gyrationsradius 7,5 nm, mittleres Teilchengewicht 900 000, mittleres Volumen 671 nm^3 und mittlere Teilchenoberfläche 717 nm^2. Aus diesen Daten und dem effektiven spezifischen Volumen (0,422 cm^3/g) wurde der Wassergehalt der Silikatteilchen zu 3% (*w*/*w*)

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* Dedicated to Prof. Dr. Dr. *Otto Kratky*, Graz, on the occasion of his 80th birthday.

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berechnet. Messungen der Röntgen-Kleinwinkelstreuung an Lösungen, die einem hydrodynamischen Feld ausgesetzt waren, zeigten, daß zumindest die größeren Teilchen in Lösung einen relativ symmetrischen Umriß haben. Basierend auf dieser Beobachtung wurde für die Berechnung einer Teilchenverteilungsfunktion eine sphärische Teilchenform angenommen. Dabei zeigte sich, daß eine einfache Funktion (etwa eine *Gauss*-Funktion) zur Beschreibung der Verteilung nicht ausreicht; stattdessen folgt die Verteilung einem Histogramm mit drei lokalen Maxima.

Introduction

Small-angle X-ray scattering is one of the most powerful methods for studying the size and shape of colloidal particles in solution. Nevertheless, the number of molecular parameters that can be extracted from one series of X-ray scattering curves is limited. Thus, it is generally not possible to analyse a polydisperse solution in some detail unless assumptions can be made regarding the shapes of the particles and the electron density fluctuations within the particles. This analysis can, however, be put on a relatively firm basis, if information about the shape can be obtained independently. In this study, on a polydisperse silicate solution, orientation experiments in a hydrodynamic field have been made in order to improve the approximations regarding the shape of the particles[1]. The main result indicates that at least the larger particles have a relatively symmetric shape. The size distribution function, based on the assumption of spherical particles, follows a histogram with particle radii from 0.70 to 15.3 nm, and it has three local maxima.

Experimental

The silicate stock solution was obtained from EKA AB, Surte, Sweden. It contained 15.0% SiO_2 and 0.355% Na_2O (by weight). X-ray small-angle scattering data were recorded with the camera developed by *Kratky* and *Skala*[2]. The scattering angle was set by an on-line Hewlett-Packard 21 MX computer, which also received and recorded the intensity data (*Wingren B. G.*, *Sjöberg B.*, *Österberg R.*, unpublished data). Monochromatization of the CuK_α radiation was achieved with a nickel filter and a pulse-height discriminator in conjunction with a proportional counter. All measurements on stationary solutions were made at 21 °C, the flow measurements at 10 °C. The absolute intensity was recorded using a Lupolen sample[3], which had been previously calibrated at the Graz Institut für Physikalische Chemie. The flow system used for producing the hydrodynamic field is exactly the same as that described elsewhere[4].

X-ray scattering data were collected for the following concentrations: 168.7, 118.6, 55.5, 32.0, 19.5, 11.0, 7.25 and 3.58 mg/cm^3. Flow experiments were performed only for the highest and lowest concentrations. Background scattering was recorded from destilled water using the same geometry as that of the silicate solutions; it was subtracted from the scattering of each silicate solution.

Results

Fig. 1 shows the series of X-ray scattering curves recorded. The plotted data, $\tilde{I}/c$ versus h, indicate a fairly pronounced interparticle scattering. These data were extrapolated to zero concentration and desmeared[5].

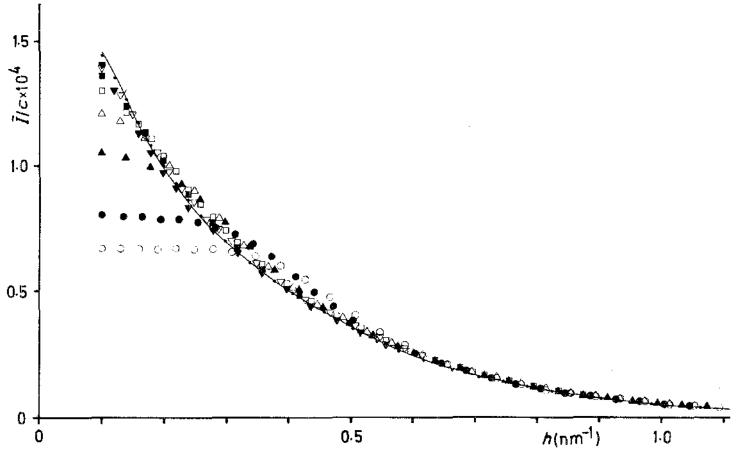

Fig. 1. Experimental data, $\tilde{I}/c$, recorded for the sodium silicate solutions. The points are the experimental values recorded for the following values of the concentration c: ○ 168.7, ● 118.6, ▲ 55.5, △ 32.0, □ 19.5, ■ 11.0, ▽ 7.25 and ▼ 3.58 mg/cm^3. The full-drawn curve was obtained by extrapolating the $\tilde{I}/c$-values to $c = 0$. The dotted curve is a theoretical curve calculated for the model described in the text. The values on the abscissa, h, are equal to $(4\pi/\lambda)\sin\theta$, where θ denotes half the scattering angle and λ the X-ray wavelength. In this figure only data for $h \leq 1.1\,\mathrm{nm}^{-1}$ are shown. In the least-squares refinement data points up to $h = 1.8\,\mathrm{nm}^{-1}$ were used

Molecular Parameters

The absolute intensity data, extrapolated to zero concentration and corrected for the collimation effect[5], yield the average radius of gyration, $\bar{R}_0 = 7.5\,\mathrm{nm}$. From the corresponding $I(0)$-value, the average particle weight was determined to be, $\bar{M} = 900\,000$; the formula described by *Kratky*[7] was used. The apparent specific volume, $\bar{v}_2$, required for these calculations, was determined via density measurements[8]; the result was $\bar{v}_2 = 0.422\,\mathrm{cm}^3/\mathrm{g}$.

The distance distribution function $p(r)$ was determined via the *Fourier* transform of $hI(h)$ using *Glatter*'s indirect method[6]; the result is shown in Fig. 2. It follows from this figure that $D_{\max}$, the largest distance within the particles is equal to 34 nm. In addition, the $p(r)$ curve shows one large maximum and at least two shoulders, a result which can either be interpreted in the form of a multidomain particle or a polydisperse solution. A multidomain particle seems quite unlikely while a polydisperse solution is in agreement with previous studies on silicate solutions. The average gyration radius was calculated from the $p(r)$ curve, the result $\bar{R}_0 = 7.2$ nm, is in good agreement with the one obtained via the *Guinier* plot (7.5 nm).

The average volume determined via *Porod*'s invariant[9] was found to be $\bar{V} = 671$ nm^3.

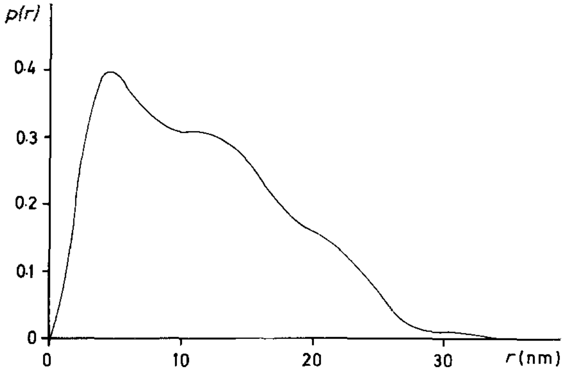

Fig. 2. Distance distribution function, $p(r)$, calculated from the small-angle X-ray data

The average particle surface area was determined from equation (1)[9]

$$\bar{S} = \pi \bar{V} \lim_{h \to \infty} h^4 I(h)/Q \tag{1}$$

where Q is *Porod*'s invariant as defined by equation (2)[9]

$$Q = \int I(h) h^2 \mathrm{d}h \tag{2}$$

The result was found to be $\bar{S} = 717$ nm^2.

From the average particle weight, $\bar{M}$, the average volume, $\bar{V}$, and the apparent partial specific volume, $\bar{v}_2$, the degree of swelling, q, was determined via the equation

$$q = (\bar{V} N_A)/(\bar{M} \bar{v}_2 10^{24}) \tag{3}$$

where N_A = *Avogadro*'s number. The result is $q = 1.06$. From this value the average water content of the particles was determined to be 3% (by weight).

Orientation Experiments

The velocity gradient in this investigation was varied from zero up to a maximum value of 51 000 s^{-1}. In spite of this relatively large gradient, the silicate solutions did not show any sign of orientation. Within the experimental errors the same scattering curve was obtained for any of the applied velocity gradients. As a result, we may conclude that at least the larger silicate particles in the solution are symmetric rather than elongated[1]. We can also conclude that the silicate particles seem to be too rigid to become deformed by the hydrodynamic field used in this investigation.

Distribution of Particle Radii in Solution

In order to analyse small-angle X-ray data obtained from a polydisperse system, certain assumptions must be made of either the size distribution or of the shape of the particles, or of both. From small-angle X-ray data alone it is not possible to differ between particle distribution and particle shape: the final result will depend on the assumptions made. From the X-ray measurements performed on the silicate solutions subjected to a hydrodynamic field it is indicated that at least the larger particles in the solution must be relatively symmetric. As the first approximation, it was therefore assumed that the silicate solutions contain a collection of spheres with equal, homogeneous electron density and attempts were made to calculate the distribution function of radii. First we assumed that the distribution function is a *Gauss*ian:

$$N(r) = C_0 \exp\{-[(r-r_0)/4\sigma]^2\} \tag{4}$$

where N is the number distribution and C_0 is a normalisation constant. The unknown parameters r_0 and σ were then refined by the method of least-squares using a computer program[10]. A search is made for the combination of parameters that corresponds to a minimum in the error square sum

$$U^2 = \sum_{k=1}^{n} w_k (\tilde{I}_k - s\tilde{i}_k)^2 / \sum_{k=1}^{n} w_k \tilde{I}_k^2 \tag{5}$$

where, $\tilde{I}_k$ is one of the n experimental slit-smeared points, w_k its weight, s a scale factor, and $\tilde{i}$ the theoretical scattering function smeared with the actual beam shape functions. However, this approach yielded values of the error-square sum that are too large; and as result a *Gauss*ian distribution function cannot explain the experimental data. Therefore, a more general approach had to be used. Here, we assumed that the distribution function can be approximated by a histogram with particle radii, r, within the interval $r_{\min} \leq r \leq r_{\max}$. The histogram is divided into ten subintervals of equal length and for the ten subintervals the heights of the bars are denoted $N_1, N_2, \ldots, N_{10}$. The twelve parameters $r_{\min}$, $r_{\max}$, $N_1, \ldots, N_{10}$ were then refined using the least-squares method as described above (cf. Ref.[10]). In this case there was a very good agreement between the smeared theoretical curve and the experimental one. The mean deviation U, where U^2 is defined by equation (5), for the 37 experimental points used in the least-squares refinement, was 0.8% and no single deviation was larger than 2%.

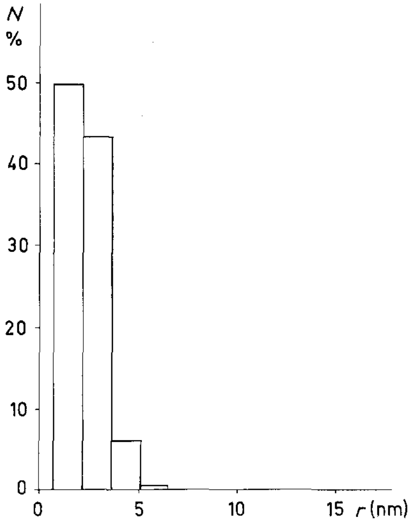

Fig. 3. The number distribution function, $N(r)$, drawn as a function of particle radius, r

The result is: $r_{\min} = 0.70\,\mathrm{nm}$, $r_{\max} = 15.3\,\mathrm{nm}$, $N_1 = 49.8$, $N_2 = 43.3$, $N_3 = 6.1$, $N_4 = 0.65$, $N_5 = 0.0000$, $N_6 = 0.0708$, $N_7 = 0.0633$, $N_8 = 0.0000$, $N_9 = 0.0213$ and $N_{10} = 0.0042\%$. This result is represented graphically in Fig. 3. It should be noted that Fig. 3 shows the number distribution function and that the number of particles with radii greater than about 6 nm are too few to be visible by the scale used in Fig. 3. These larger particles can, however, easily be detected by the small-angle X-ray method since the scattered intensity (at zero angle) is proportional to the square of the number of excess electrons per particle. A distribution based on particle weight is shown in Fig. 4; this distribution, as expected, shows particles with larger radii than those of Fig. 3. A comparison between experimental points and the theoretical curve calculated from the histogram in Fig. 3 is shown in Fig. 1.

It should be noted that a great number of other models, both regarding particle shape and distribution functions, have also been tested. For instance, when the particles were initially assumed to have ellipsoidal shapes they changed during the refinement into spheres. All these other models yield error-square sums which are more than 50 times greater than that obtained for the histogram represented in Fig. 3.

Discussion

The results presented in the previous section indicate that, within the resolution of small-angle X-ray scattering, there are good reasons to assume that the silicate particles in the solution have spherical symmetry. As a result, the intensity cannot be explained by a solution of monodisperse particles. An analysis of the data was therefore made in the form of the distribution of the particle radii assuming homogeneous electron density for the particles. Various approaches were used in this analysis. A satisfactory result was only obtained when assuming that the particle size distribution follows a histogram (Figs. 3 and 4). Fig. 4 shows that the main fraction of particles has radii between 2.2 and 3.6 nm; it corresponds to 55% (by weight) of the total solute mass. The largest particle indicated in Fig. 4, on the other hand, has a much larger radius, about 15.3 nm. Within the experimental error, the largest dimension, 30.6 nm, of the largest particle is in good agreement with the $D_{\max}$-value of 34 nm obtained via the $p(r)$ curve in Fig. 2.

The number distribution of Fig. 3 makes it possible to independently compare the particle parameters reported in the previous section, such as the average volume, $\bar{V}$, the average surface area, $\bar{S}$, and the average radius of gyration, $\bar{R}_0$. Using equations (11)-(14) in Ref.[11], we obtain $\bar{V} = 720\,\mathrm{nm}^3$, $\bar{M} = 960\,000$, $\bar{S} = 640\,\mathrm{nm}^2$ and $\bar{R}_0 = 8.2\,\mathrm{nm}$. The agreements for all the paramters are better than ten percent, and this suggests that the description of the particles in the form of spheres is probably a fairly correct description of their shapes. The deviation between the surface area $\bar{S}$, calculated from the distribution function (640 nm^2) and the experimental value (717 nm^2) may be due to the fact that the calculated value assumes a mathematically exact sphere with a smooth surface. One might expect the real surface of the particles to be relatively irregular which should yield a larger surface area than a smooth sphere. We should also keep in mind that the assumption regarding homogeneous electron density is only approximately correct and it is difficult to estimate the possible contribution to the intensity from the internal structure.

Of special interest is that the particle weight distribution has several local maxima, Fig. 4. Particles with radii about 7 and 11.5 nm do not seem to exist at all, whereas maxima are obtained for 2.9, 10.2, and 13.2 nm. Such a polydisperse solution with a non-continuous variation of particle radii agrees qualitatively with one maximum and two shoulders in the $p(r)$ curve (Fig. 2). Such a $p(r)$ curve is compatible with the existence of at least three different structural domains for the silicate particles in solution, and a calculation of $p(r)$ for the particle distribution shown in Fig. 3 indicates that it essentially describes the experimental one.

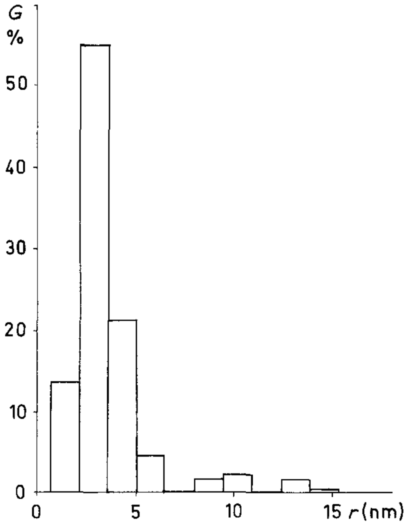

Fig. 4. The weight distribution function, $G(r)$, drawn as a function of particle radius, r

Although the present analysis of the data yields a distribution of radii for the particles in solution, it does not make it possible to calculate the parameters of one particular particle via a simple formula. An estimate regarding the minimum amount of silicate which has to be added to one particular particle in order to form a larger one, indicates that it corresponds to a particle with a radius of about 3 nm. It should finally be noted that the present result indicating a non-continuous distribution function of radii is surprising since previous studies on particle size distribution of silicate solutions have indicated quite different distribution functions; for instance, various Ludox samples give distribution curves with only one maximum[12].

Acknowledgements

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