

Attractions in Sterically Stabilized Silica Dispersions

IV. Sedimentation

J. W. JANSEN, C. G. DE KRUIF, AND A. VRIJ

*Van't Hoff Laboratory for Physical and Colloid Chemistry, University of Utrecht,
Padualaan 8, 3584 CH Utrecht, The Netherlands*

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The concentration dependence of the sedimentation velocity of sterically stabilized silica particles is measured. With toluene as a solvent this dependence decreases with decreasing temperature. This observation is explained in terms of attractions between the particles. The measured sedimentation coefficients show a behavior in accordance with theory. The temperature dependence parallels that of the osmotic second virial coefficient as measured with light scattering. © 1986 Academic Press, Inc.

1. INTRODUCTION

Knowledge about the dynamic properties of concentrated colloidal dispersions is of great importance in technology (1, 2) and consequently there is also increasing interest in the theory of these dispersions (3). Many dispersions encountered in technology and nature have an extremely complicated composition and therefore the interactions between the colloidal particles are complex too. This makes it very difficult to test theories on the (dynamic) properties of these dispersions. In our laboratory a model system has been developed which consists of spherical monodisperse silica particles of various sizes. They are rendered organophilic by grafting of a layer of short alkane chains onto the surface (4). The static interaction between these particles is relatively simple. Since the particles are not charged and ions do not form easily in the low-dielectric-constant organic solvents, charge interaction can be neglected. London-van der Waals attractions between the particle cores are negligible too. This is in accordance with the small difference between the refractive index of particle and (organic) solvent (5). The only important interaction is therefore via the chains on the surface. The free energy change when two particles come into contact is determined

by the balance between the loss of entropy of the chains and the enthalpic interaction. This enthalpic interaction is therefore via the chains on the surface. The free energy change when two particles come into contact is determined by the balance between the loss of entropy of the chains and the enthalpic interaction. This enthalpic interaction is in its turn determined by the balance between the interactions between two chain segments and between solvent molecules and chain segments. If the latter are highly favorable, i.e., they promote stabilizing, the quality of the solvent is said to be good. The net interaction will be temperature dependent, mainly because of the entropy term.

It turned out that silica particles dispersed in cyclohexane behave as a so-called hard sphere system (6, 7). In other solvents such as toluene the interaction can be made attractive by lowering the temperature (5, 8). In this paper we report on the concentration dependence of the sedimentation velocity of these (attractive) silica particles. Results will be related to measurements of the second virial coefficient of this system (8).

2. THEORY

For low concentrations (volume fractions $\phi < 0.05$) Batchelor (9) derived an expression

for the concentration dependence of the sedimentation velocity of hard spheres in a Newtonian fluid (Eq. [1]):

$$S = S_0(1 + K_s\phi). \quad [1]$$

Here ϕ is the volume fraction and K_s is given by [9]

$$K_s = \frac{3}{a^2} \int_a^\infty (g(r) - 1)rdr - \frac{1}{2} + \frac{1}{a^3} \int_{2a}^\infty g(r) \times \left[A(r) + 2B(r) - 3\left(1 + \frac{a}{2}\right) \right] r^2 dr. \quad [2]$$

Here a is the radius of the sphere and $g(r)$ the pair distribution function which for low concentrations is equal to $e^{-V(r)/kT}$ with $V(r)$ the interaction potential; $A(r)$ and $B(r)$ are the mobility function of two spheres parallel and perpendicular to the sedimentation driving force. For a hard sphere repulsive potential where $g(r) = 1$ for $r > 2a$ at low concentrations, K_s is found to be -6.55 .

In addition to hard sphere interactions Batchelor also considered other types of interaction. For short-range attractions the $g(r)$ of hard spheres is supplemented by a term which accounts for the adsorption of particles onto the central particle. The number of particles adsorbed is given by

$$\Gamma = 4\pi n \int_{2a}^\infty (g(r) - 1)r^2 dr \quad [3]$$

which is greater than zero for attractive interactions. The adsorbed amount is proportional to the volume fraction of the particles $\Gamma = \alpha\phi$. If all adsorbed particles are placed at $r = 2a$, $g(r)$ becomes

$$g(r) = g(r)_{HS} + \alpha \frac{a}{12} \delta(r - 2a) \quad [4]$$

where

$$\delta(r - 2a) = \infty \quad \text{for } r = 2a \\ = 0 \quad \text{for } r \neq 2a$$

and

$$\int \delta(r - 2a)f(r)dr = f(2a).$$

Using this $g(r)$ in Eq. [2], K_s for attractive spheres becomes

$$K_s = -6.55 + 0.44\alpha. \quad [5]$$

From this equation it can be seen that with a fixed volume fraction attractive spheres will settle faster than hard spheres. Qualitatively this can be understood because solvent in the vicinity of a sedimenting particle is dragged down. To keep the net flux zero, solvent far away from this particle must flow back. Other particles near this particle will profit from the downward flow. Because with attractions more particles will be near the central particle than with repulsive interactions the sedimentation velocity will be higher. Alternatively one can say that when attractions are present the dispersion contains temporary doublets, the drag coefficient of which is smaller; the mean sedimentation velocity is therefore higher.

Previously (5) we described the interaction potential between two particles as a hard sphere repulsion to which a square well was added. $V(r)$ is thus

$$V(r) = \infty \quad r < 2a \\ = -\epsilon \quad 2a < r < 2a + \Delta \\ = 0 \quad r > 2a + \Delta.$$

The depth of the well, ϵ , depends on temperature:

$$\epsilon = L \left(\frac{\theta}{T} - 1 \right) kT; \quad T \leq \theta \\ \epsilon = 0; \quad T > \theta \quad [6]$$

The width Δ is small compared to the particle diameter, say, about 0.1 nm (i.e., 1/20th of the chain length). With this interaction potential α is calculated to be

$$\alpha = 12 \frac{\Delta}{a} (e^{L(\theta/T)-1} - 1). \quad [7]$$

Since the interaction potential also determines the static properties of the macrofluid the coefficient α also appears in the expression for the second virial coefficient. B_2 for particles with an attractive square well is

$$B_2 = q \left\{ 4 - 6 \frac{\Delta}{a} (e^{L(\theta/T)-1} - 1) \right\} \quad [8]$$

as is derived in Ref. (8). In Eq. [8] q is the specific interaction volume ($\phi = qc$); for hard spheres $B_2 = 4q$. It can thus be seen that the

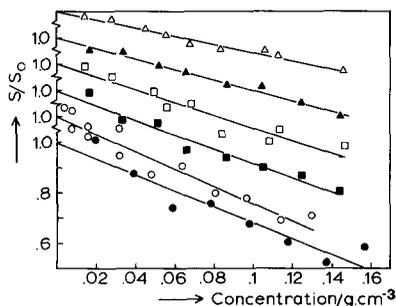


FIG. 1. Sedimentation constants of particles SJ9 as a function of concentration. ●, In cyclohexane at 25.0°C; ○, in toluene at 25.0°C; ■, 20.0°C; □, 14.8°C; ▲, 12.1°C; and △, 10.0°C.

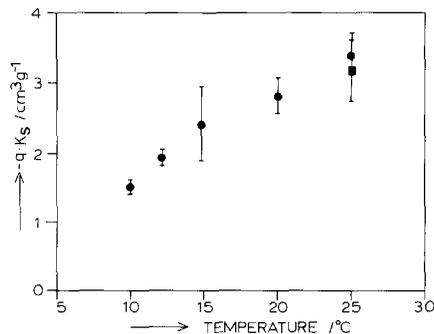


FIG. 2. Values of K_s as a function of temperature.

attractive part of B_2 is equal to $q\alpha/2$. The variation of $2B_2/q$ and of $-K_s/0.44$ with temperature will thus be the same.

3. EXPERIMENTAL

3.1. Materials and Method

For the synthesis of the silica particles (code SJ9) we refer to (4). The solvents used, cyclohexane and toluene (both Baker p.a.), were used as received. Sedimentation velocity experiments were conducted with a Beckmann Spinco (Model E) analytical ultracentrifuge, using cells of various lengths. The sedimentation boundary was observed with scanning absorption optics and with photographs of the Schlieren image of the samples. The top of the Schlieren peak was taken as the position of the sedimentation boundary. The latter technique gave the more accurate data. Care was taken to keep the temperature constant within 0.1°C and the temperature was measured during the sedimentation run.

3.2. Characterization of the Silica Particles

The size of the particles was measured using two techniques. Transmission electron microscopy gave a radius of 31 nm and a width of the distribution of 13%. The diffusion coefficients (measured with photon correlation spectroscopy) of the particles in cyclohexane and in toluene are 6.6 and $10.5 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ resp., resulting in radii 36.9 and 37.2 nm. The pycnometric density of a dispersion of known concentration yielded a particle density of $1.75 \pm 0.02 \text{ g} \cdot \text{cm}^{-3}$. Elemental analysis showed a weight percentage of 11.7% organic material, resulting in a chain coverage of 5.7 chains/nm².

4. RESULTS AND DISCUSSION

Dispersions were made of particles SJ9 in cyclohexane and in toluene by dissolving dried silica. Concentrations used were in the range 0.01 – $0.15 \text{ g} \cdot \text{cm}^{-3}$. Sedimentation coefficients s (divided by the intercept s_0) are plotted in

TABLE I

Values of the Intercepts and Slopes in Fig. 1, Viscosity of Solvent, Density Difference between Particle and Solvent, and Calculated Radius (Eq. [9])

Solvent	Temperature (°C)	$q \cdot K_s$ (cm ³ ·g ⁻¹)	s_0 (10 ⁻¹⁰ s ⁻¹)	Viscosity (cSt)	Δd (g·cm ⁻³)	Radius (nm)
Cyclohexane	25.0	-3.17 ± 0.47	2.38 ± 0.11	0.898	0.989	31.2
Toluene	25.0	-3.40 ± 0.31	3.86 ± 0.07	0.552	0.900	32.6
	20.0	-2.82 ± 0.25	3.59 ± 0.08	0.583	0.896	32.4
	14.8	-2.42 ± 0.54	3.38 ± 0.08	0.625	0.891	32.7
	12.1	-1.94 ± 0.12	3.24 ± 0.03	0.650	0.888	32.7
	10.0	-1.51 ± 0.11	3.18 ± 0.03	0.670	0.887	32.9

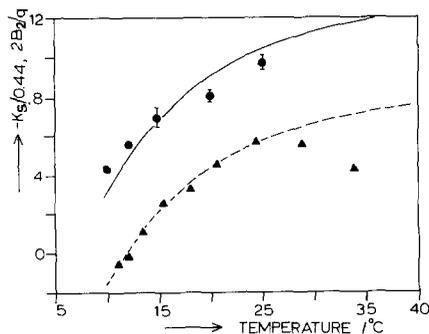


FIG. 3. A comparison of the values of (●) $-K_s/0.44$ and (▲) $2B_2/q$. The continuous curve is the same as the dashed one, but shifted in the vertical direction by 4.6 units.

Fig. 1 for the two solvents. The samples in toluene are made to sediment at temperatures ranging from room temperature down to 0.5°C above the temperature at which phase separation occurs. Values of the slopes of s versus c at a fixed temperature are listed in Table I and plotted versus temperature in Fig. 2.

From the data in Table I it can be seen that both the intercept and the slope change with temperature. The variation of the intercept (which is the sedimentation coefficient of a single particle) with temperature can be attributed entirely to the change in viscosity (η) of the solvent and the density difference (buoyancy) of the particle and solvent (Δd). Using Stokes' Law one finds for s_0

$$s_0 = \frac{2 \Delta d a^3}{9 \eta a_\eta} = \frac{2 \Delta d}{9 \eta} a_s^2. \quad [9]$$

From the intercept found for cyclohexane and toluene the particle radii were calculated (Table I) and turned out to be the same. This radius a_s (calculated with Eq. [9]) is somewhat smaller than the hydrodynamic radius. This is because in the derivation of Eq. [9] the weight of the particles (proportional to a^3 where a is the "dry" radius) is divided by the hydrodynamic radius a_η . Since the former is smaller than the latter, a_s is smaller than a and a_η .

The slopes in Fig. 1 for samples in toluene become less negative toward lower temperatures. This is attributed to the development of

attractions. Using our model (Eq. [7]) we could make a fit to obtain L and θ , but unfortunately the errors in the slopes are too large. As is shown in the theoretical part K_s and the second virial coefficient are related. In Fig. 3 we plotted $2B_2/q$ as found in Ref. (8) (using $a = 35$ nm, $\theta = 353$ K, and $L = 22.8$) and $-K_s/0.44$. The curve drawn through the experimental points is the same as for $2B_2/q$, but shifted in the vertical direction by 4.6 units. This curve describes the sedimentation experiments satisfactorily and the variation of the slope can thus be described with the same model as the variation of B_2 . In estimating K_s and s_0 we used concentrations of up to $0.15 \text{ g} \cdot \text{cm}^{-3}$, although the theory of Batchelor is valid for low volume fractions only. Even so, it is gratifying that the variation of K_s with temperature compares reasonably with the static interaction (i.e., B_2).

In conclusion we point out that more theoretical work should be done on dispersions with attractive interactions. Experiments on other silica dispersions and higher concentrations are planned and results will be published in subsequent papers.

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