

Determination of the solvation film thickness of dispersed particles with the method of Einstein viscosity equation

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Abstract: The dispersion of a solid particle in a liquid may lead to the formation of solvation film on the particle surface, which can strongly increase the repulsive force between particles and thus strongly affect the stability of dispersions. The solvation film thickness, which varies with the variation of the property of suspension particles and solutions, is one of the most important parameters of the solvation film, and is also one of the most difficult parameters that can be measured accurately. In this paper, a method, based on the Einstein viscosity equation of dispersions, for determining the solvation film thickness of particles is developed. This method was tested on two kinds of silica spherical powders (namely M1 and M2) dispersed in ethyl alcohol, in water, and in a water-ethyl alcohol mixture (1:1 by volume) through measuring the relative viscosity of dispersions of the particles as a function of the volume fraction of the dry particles in the dispersion, and of the specific surface area and the density of the particles. The calculated solvation film thicknesses on M1 are 7.48, 18.65 and 23.74 nm in alcohol, water and the water-ethyl alcohol mixture, 12.41, 12.71 and 13.13 nm on M2 in alcohol, water and the water-ethyl alcohol mixture, respectively.

Key words: solvation film; viscosity; film thickness; Einstein viscosity equation

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1 Introduction

Materials in a colloidal state are frequently preferred in industrial processing operations (*e.g.*, printing inks, toners, paints, skin creams, blood substitutes, gels used as drug-delivery systems, *etc.*) because their large surface areas per unit volume enhance the chemical reactivity, adsorptive capacity, heat transfer rate, and so on. A good dispersion of colloidal is very important for these materials, in other words, these materials need sustain in good dispersion stability [1].

According to the DLVO theory [2], the dispersion stability of colloidal suspensions is due to the existence of energy barrier which arises as a result of the electrical double layer force and the van der Waals forces. Usually, if an electrolyte is added to a colloidal suspension, causing marked compression of the electrical double layer around colloidal particles, coagulation will occur. However, this theory fails to apply to some lyophilic particle suspensions, in which no particle coagulation occurs even in a moderately concen-

trated salt solution [3]. For instance, it has been found that silica suspensions exhibit a high dispersion stability through whole pH, even at its point of zero charge. Derjaguin and Churaev [4] attributed these observations to the solvation film of water (also called hydration film) on silica surfaces resulting in strong disjoining pressure between the particles, as shown in **figure 1**. And they thus proposed the extended DLVO, which takes hydration force into account besides the electrical double layer and van der Waals forces.

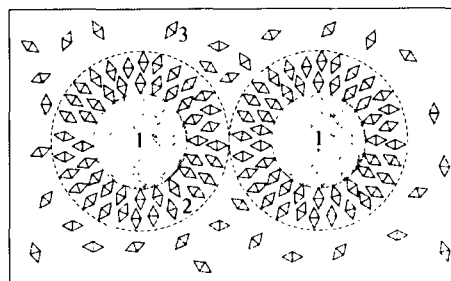


Figure 1 Effect of the solvation film of dispersed particles on the dispersion's stability. 1—particle; 2—solvation film; 3—solvent molecular.

NMR (nuclear magnetic resonance), IR (infrared) and UV (ultraviolet) spectroscopes, X-ray crystallography, surface force apparatus (SFA), and atomic force microscope (AFM) have been used to determine the solvation film structure and solvation forces [5-9]. The experimental results showed that the magnitude of solvation force was much larger than those of the electrical double layer and van der Waals forces, which well explained the high stability of silica fines in aqueous solutions.

However, most of these experiments focused their attention on the solvation force between particles, but neglected the effects of the solvation film thickness and structure. Only a few reports [10-11] touched the determination of the solvation film thickness with the blow-off method which was developed in the 1950s.

In the present study, a new method based on the Einstein viscosity equation of dispersion for determination of the solvation film thickness on spherical particles in liquids is presented. The method can calculate the solvation film thickness from the data of dispersion viscosity, the volume fraction of dry particles, the specific surface area and the density of the particles. Two kinds of silica spheres (namely M1 and M2) were used here to test the new method in ethyl alcohol, water, and a water-ethyl alcohol mixture (1:1 by volume) in the present work.

2 Einstein viscosity equation of dispersions

The presence of a colloidal size particle in the liquid increases the viscosity because of its effect on the flow pattern. In 1906 Albert Einstein [1] published his first derivation of an expression for the viscosity of a dilute dispersion of solid spheres (so called Einstein viscosity equation) as following:

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi_p \quad (1)$$

where the quantity η/η_0 is termed the relative viscosity, η and η_0 are the viscosities of the dispersion and of the liquid medium respectively, ϕ_p is the volume fraction of dispersed particles.

It can be seen clearly from equation (1) that the relative viscosity linearly increases with the increasing of the volume fraction of the dispersed particles with a slope of 2.5. But the equation is limited to the concentration below $\phi_p=0.10$. For high volume fractions of dispersed particles, Einstein's equation might be extended by retaining terms higher than the first order in the power series as shown in equation (2):

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi_p + k_1\phi_p^2 + \dots \quad (2)$$

It should be noted that the Einstein's equation is

based on the most important postulate that dispersed particles are rigid spheres with no solvation film on their surfaces [1].

3 Theory derivation from the Einstein viscosity equation to the solvation film thickness

Einstein's theory is based on the hypothesis of unsolvated spheres, but the fact is that a solid particle dispersed in a liquid may lead to the formation of solvation film on its surface. The solvation film can swell the particle volume above its dry volume, as shown in **figure 2**. This swelling of the volume increases the viscosity of the dispersion above the value the viscosity would have if no solvation film formed.

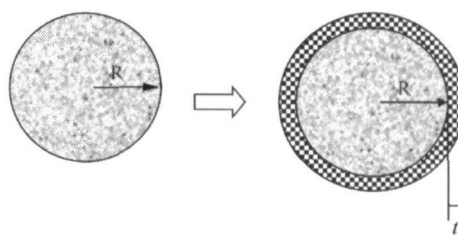


Figure 2 Schematic diagram of the solid sphere with and without solvation film.

So equation (1) should be changed into a modified one as:

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi_T \quad (3)$$

where ϕ_T is the total volume fraction of dispersed particles and their solvation films. If only the dry volume fraction of particles (ϕ_p) which carry solvation films is used as the total volume (ϕ_T) of the particles, the measured values of the viscosity of the dispersion will not obey Einstein's equation. Thus the slope of a graph of η/η_0 vs. ϕ_p will be different from 2.5. It is the difference of slope values that can provide us enough information for deriving the solvation film thickness as following.

Before derivation, two assumptions are made for a dispersion of rigid spheres solvated by the liquid: (a) solvation films contribute to the increase in viscosity of dispersions in the same way as the solid spheres described by Einstein's equation; (b) the thickness of solvation films is the same on every chemically similar spherical particle in a given dispersion.

According to the assumptions, the total volume of solvated spheres (V_T) in a liquid should be the sum of volume of dry spherical particles (V_p) and that of solvation films (V_f):

$$V_T = V_p + V_f \quad (4)$$

Thus the total volume fraction of solvated spheres

(ϕ_T) which obeys to Einstein's equation will include both the volume fraction of dry spherical particles (ϕ_P) and that of solvation films (ϕ_f):

$$\phi_T = \phi_P + \phi_f \quad (5)$$

The latter two volume fractions are given by

$$\phi_P = \frac{V_P}{V} \quad (6)$$

$$\phi_f = \frac{V_f}{V} \quad (7)$$

where V is the volume of the dispersion. The volume of solid particles is

$$V_P = \frac{M}{\rho} \quad (8)$$

where M is the mass of the solid particles of dispersion and ρ the density of particles.

According to figure 2, equation (8) can be rewritten as

$$V_P = \frac{4}{3} \pi R^3 \quad (9)$$

and

$$V_T = \frac{4}{3} \pi (R + t_f)^3 \quad (10)$$

Assuming $t_f = \lambda R$, then equation (10) can be rearranged as

$$V_T = (1 + \lambda)^3 V_P \quad (11)$$

thus

$$\phi_T = (1 + \lambda)^3 \phi_P \quad (12)$$

Now, the Einstein viscosity equation of solvated sphere dispersions can be expressed as

$$\frac{\eta}{\eta_0} = 1 + 2.5(1 + \lambda)^3 \phi_P \quad (13)$$

Equation (13) indicates that a graph of η/η_0 against ϕ_P should yield a straight line for a given dispersion of

solid spheres with an intercept = 1 and

$$\text{Slope} = k = 2.5(1 + \lambda)^3 \quad (14)$$

From equation (14), we can get

$$\lambda = \sqrt[3]{0.4k} - 1 \quad (15)$$

while

$$\lambda = \frac{t_f}{R} \quad (16)$$

and R can be calculated from the specific surface area (A_{sp}) and the density (ρ) of the particles:

$$R = \frac{3}{\rho A_{sp}} \quad (17)$$

So the solvation film thickness of the solvated rigid spheres can be calculated from combining the equations (15)-(17):

$$t_f = (\sqrt[3]{0.4k} - 1) \frac{3}{\rho A_{sp}} \quad (18)$$

In equation (18), A_{sp} and ρ are the physical properties of solid spheres and t_f is closely correlated with the interaction between liquid molecules and solid surfaces, all of which are independent on the volume fraction of dry solid spheres (ϕ_P) in dilute dispersions where Einstein's equation applies. In other words, the three parameters are constants for a given spherical-particle dispersion. So t_f can be calculated from equation (18), since A_{sp} , ρ and k can be obtained from the experimental determination.

3 Experiment

3.1 Materials

Two kinds of spherical silica powder were used in this work. One powder, named M1, was obtained from Shanghai Zhengmei Sub-nanoscale Material Manufacturing Co. Ltd. (Shanghai, China), the size range is 0.5-5 μm . Another silica powder, named M2, was obtained from SIGMA-Aldrich Co. (St. Louis, USA), the size range is 10-15 nm. The physical properties of M1 and M2 are listed in table 1.

Table 1 Physical properties of silica spheres M1 and M2

Particles	Specific surface area / ($\text{m}^2 \cdot \text{g}^{-1}$)	Density / ($\text{g} \cdot \text{cm}^{-3}$)	Ratio of spheres	Specific surface average diameter / nm
M1	2.2418	2.585	>95%	1035.37
M2	189.0357	2.550	>95%	12.45

Ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) was obtained from J.T. Baker (Xalostoc, Mexico) with a purity of 99.90%. The water used in this work was first distilled and then passed through a mixed ion-exchange resin bed, with a conductivity less than 1 $\mu\text{S}/\text{cm}$. The mixture of water-ethyl alcohol was prepared by mixing equal volumes of alcohol and water.

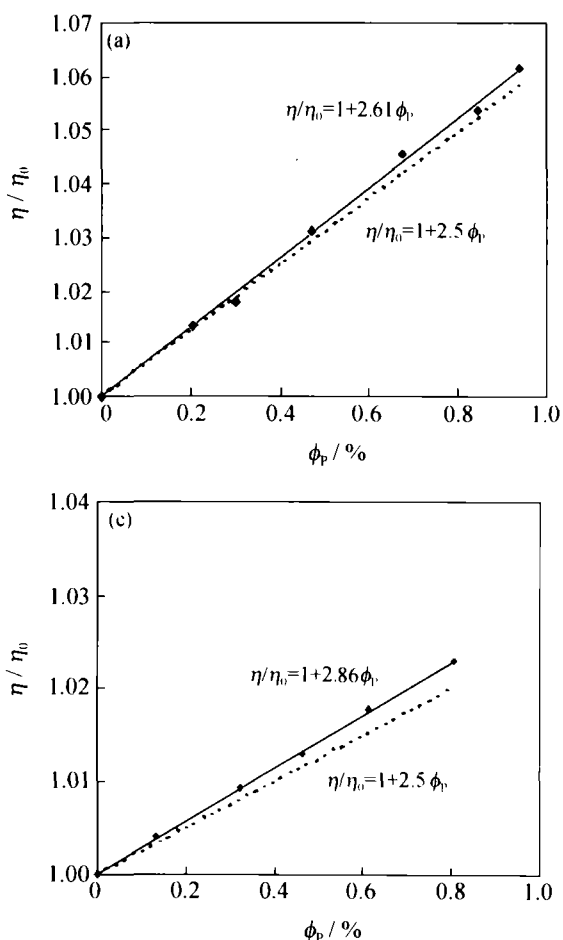
3.2 Measurements

A Physica Rhrolab MC-1 concentric cylinder rheometer (Physica Messtechnik GmbH, Ostfildern, Germany) was used to determine the viscosities of the silica dispersions. The torque resolution is 0.01 mN·m. The temperature control system permits the viscosity measurement to be performed at a fixed temperature

with a precision of $\pm 0.05^\circ\text{C}$ and all viscosity experiments were done at 20°C . The specific surface areas (A_{sp}) of M1 and M2 were determined with a Micromeritics ASAP 2000 specific surface area meter (Micromeritics Corporation, Norcross, GA, USA). The density of the spheres (ρ) was obtained through the measurements with a 50 mL specific gravity bottle.

4 Results and discussion

The relative viscosities of the M1 dispersions in



ethyl alcohol, water, and the water-ethyl alcohol mixture as a function of the volume fraction of “dry” solid spheres (ϕ_p) are shown in **figure 3**. While **figure 4** shows the relative viscosities of the M2 dispersions in ethyl alcohol, water, and the water-ethyl alcohol mixture as a function of the volume fraction of “dry” solid spheres (ϕ_p). Since the measured viscosities increase linearly with the increasing of volume fraction of dry particles as shown in the figures, six different linear equations were regressed as following:

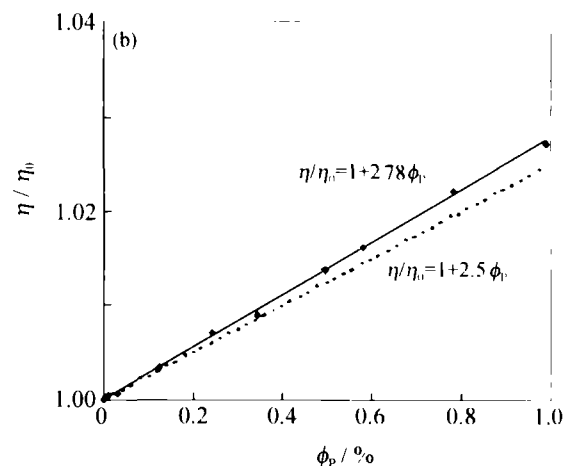
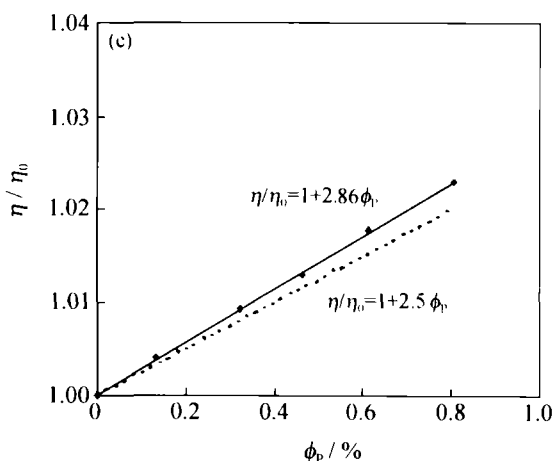


Figure 3 Relative viscosities of the dispersions of the silica spheres M1 in ethyl alcohol (a), in water (b), and in the water-ethyl alcohol mixture (c) as a function of the volume fraction of the spheres.



$$\eta/\eta_0 = 1 + 2.61\phi_p \quad (19)$$

$$\eta/\eta_0 = 1 + 2.78\phi_p \quad (20)$$

$$\eta/\eta_0 = 1 + 2.86\phi_p \quad (21)$$

for the M1 dispersions in ethyl alcohol, water, and the water-ethyl alcohol mixture, respectively.

$$\eta/\eta_0 = 1 + 67.05\phi_p \quad (22)$$

$$\eta/\eta_0 = 1 + 70.39\phi_p \quad (23)$$

$$\eta/\eta_0 = 1 + 75.13\phi_p \quad (24)$$

for the M2 dispersions in ethyl alcohol, water, and the water-ethyl alcohol mixture, respectively.

Figures 3 and 4 also show dashed lines with a slope of 2.5 which is the “theoretical” slope of Einstein’s equation without considering the effect of solvation

film. The differences between “experimental” and “theoretical” slopes can be attributed to the presence of solvation films on dispersed particles. With the experimental results from the viscosity measurement as shown in equations (19)-(24), together with the specific surface area (A_{sp}) and the density (ρ) of silica spheres, the solvation film thickness was evaluated from equation (18), and the results are listed in **table 2**. It can be seen from table 2 that the calculated solvation film thicknesses on M1 are 7.48, 18.65 and 23.74 nm in ethyl alcohol, water and the water-ethyl alcohol mixture, 12.41, 12.71 and 13.13 nm on M2 in ethyl alcohol, water and the water-ethyl alcohol mixture, respectively. The calculated solvation film thickness of water on M1 and M2 is of the same order as the determined one by the blow-off method for hydration layers on clean quartz [4, 11]. The difference of the

thickness between silica spheres M1 and M2 in ethyl alcohol (7.48 vs. 12.41 nm), in water (18.65 vs. 12.71 nm), and in the water-ethyl alcohol mixture (23.74 vs.

13.13 nm) may be because of the difference of their surface characters or their size (517.68 vs. 6.22 nm), which need more deep investigation in our late work.

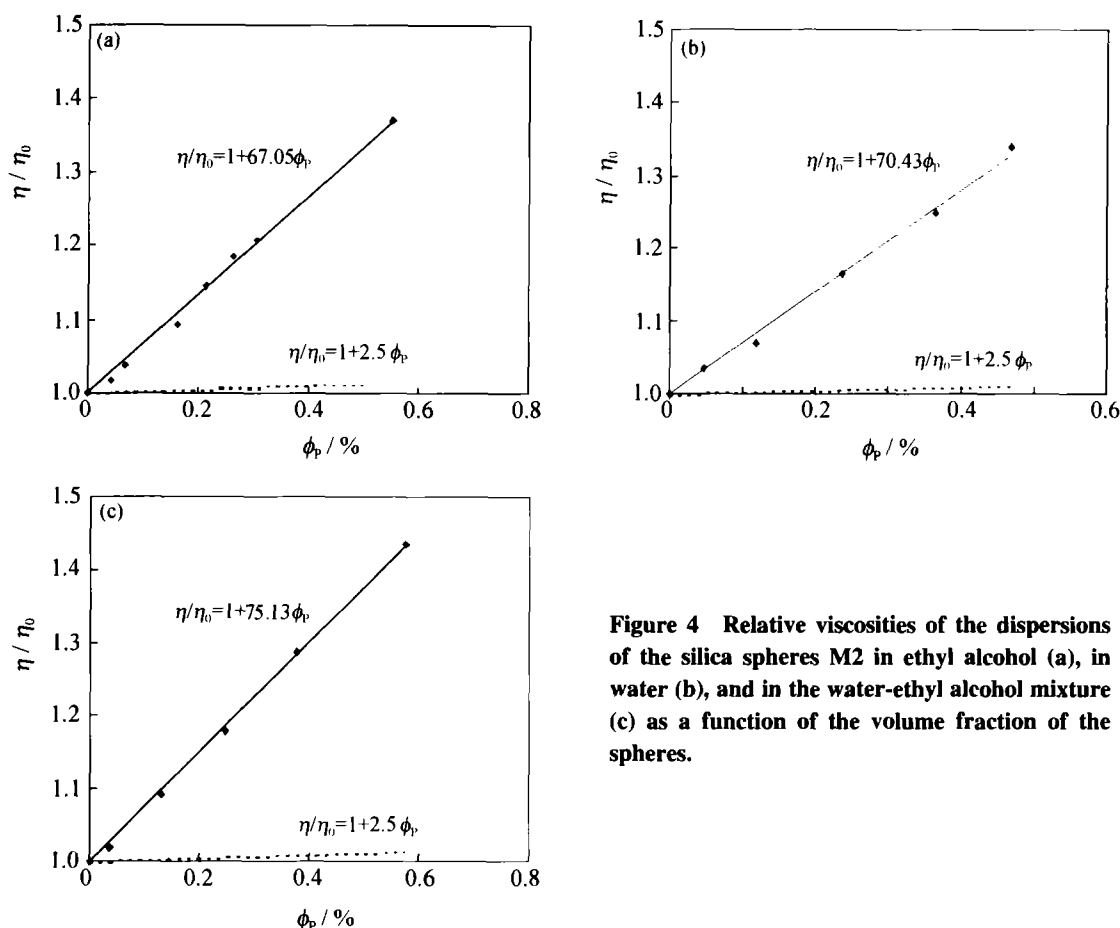


Figure 4 Relative viscosities of the dispersions of the silica spheres M2 in ethyl alcohol (a), in water (b), and in the water-ethyl alcohol mixture (c) as a function of the volume fraction of the spheres.

Table 2 Thicknesses of solvation film on M1 and M2 silica spheres in ethyl alcohol, in water and in the water-ethyl alcohol mixture

Parameter	M1 silica spheres			M2 silica spheres		
	Alcohol	Water	Mixture	Alcohol	Water	Mixture
Specific surface area / (m ² ·g ⁻¹)	2.2418	2.2418	2.2418	189.0357	189.0357	189.0357
Radius / nm	517.68	517.68	517.68	6.22	6.22	6.22
Density / (g·cm ⁻³)	2.585	2.585	2.585	2.550	2.550	2.550
Slope	2.61	2.78	2.86	67.05	70.39	75.13
Film thickness / nm	7.48	18.65	23.74	12.41	12.71	13.13

5 Conclusions

The new method, based on the Einstein viscosity equation, can calculate the solvation film thickness of solid particles in dispersions, according to the determination of the three measurable parameters such as the dispersion viscosity, the specific surface area of particles, and the density of particles. The viscosity method may lead to an improved understanding of the solvation film on particles in dispersions of importance in colloid science, biology, material science, etc.

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