

Effect of pH on the Rheological Properties of a Silica Hydrosol

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Abstract

The viscosity of a silica hydrosol is studied as a function of the volume fraction of silica for pHs from 2 to 11 using a capillary flow viscometer. The experimental curves depend on the pH of the sol and exhibit a discrepancy with the behaviour predicted from theoretical expressions. An adsorbed layer must exist on these colloidal particles (equivalent spherical radius of 87–88 Å) which increases the volume fraction of the dispersed phase. The hydrodynamic radius r_H including the thickness of the layer is calculated from the viscometric data. The values obtained at pH 2 and 9.7 are 94–98 and 110–115 Å respectively. These analyses are used to explain previously reported results on the variation of gel packing density as a function of pH. The hydrodynamic radius of the particles is also determined from measurements on dilute sols using quasi-elastic light scattering. At pH 9.7, the measured value, 120 Å, is close to that previously calculated. The highest measured r_H , 130 Å, is obtained at pH 2. An explanation is proposed to account for the difference from the calculated value.

Die Viskosität einer SiO₂-kolloidalen Lösung in Wasser wurde mit einem Kapillarviskosimeter (Ubbelohde Röhre) für pH-Werte von 2–11 in Abhängigkeit des SiO₂-Volumenanteils untersucht. Die experimentellen Ergebnisse hängen vom pH des Sols ab und weichen vom theoretisch vorhergesagten Verhalten ab. Auf diesen kolloidalen Teilchen mit einem äquivalenten Kugelradius von 87–88 Å muß eine adsorbierte Schicht vorliegen, die den Volumenanteil der dispergierten Phase erhöht. Der hydrodynamische

Radius r_H , der diese Schicht berücksichtigt, wurde aus den Viskositätsdaten berechnet. Bei pH 2 und 9.7 ergeben sich Werte von 94–98 bzw. 110–115 Å. Diese Überlegungen wurden zur Erklärung früherer Ergebnisse über die Änderung der Gel-Packungsdichte in Abhängigkeit vom pH-Wert herangezogen. Der hydrodynamische Radius der Teilchen wurde auch durch quasielastische Lichtstreuungsmessungen an verdünnten Sols bestimmt. Bei einem pH-Wert von 9.7 liegt der gemessene Wert von 120 Å nahe bei dem obig berechneten Wert. Der höchste Wert für r_H wurde bei pH 2 gemessen und liegt bei 130 Å. Auf die Abweichung zum berechneten Wert wird eingegangen.

La viscosité d'un hydrosol de silice est étudiée en fonction de la fraction volumique de silice pour des valeurs de pH comprises entre 2 et 11, en utilisant un viscosimètre à écoulement. Les courbes expérimentales évoluent avec le pH du sol et montrent un écart par rapport au comportement attendu à partir des expressions théoriques. Une couche adsorbée doit exister à la surface de ces particules colloïdales (rayon de sphère équivalente: 87–88 Å), qui accroît la fraction volumique de phase dispersée. Le rayon hydrodynamique r_H qui intègre l'épaisseur de cette couche est calculé à partir des données viscosimétriques. Les valeurs obtenues à pH 2 et 9.7 sont respectivement, de 94–98 et 110–115 Å. Ces analyses sont utilisées pour expliquer des résultats rapportés antérieurement sur la variation de densité du gel en fonction du pH du sol. Le rayon hydrodynamique des particules est également déterminé à partir de mesures sur les sols dilués en utilisant la diffusion quasi-élastique de la lumière. A pH 9.7, la valeur mesurée, 120 Å, est proche de celle préalablement calculée. La

valeur maximale pour r_H mesuré, 130 Å, est obtenue à pH 2. Une explication est proposée pour rendre compte de la différence entre cette valeur et la valeur calculée.

1 Introduction

Silica hydrosols can be synthesized with particles of controlled size and are used for many industrial applications¹ such as ceramic binders. The textural properties as well as the mechanical properties of the final material depend on the stability and rheological characteristics of the sol. Silica sols show a distinctive behaviour compared with dispersions of other oxides: they are stable at a pH value ~ 10 , corresponding to a high zeta potential, value, but they exhibit an unusual stability maximum for the isoelectric point of SiO₂ (pH ~ 2).¹ In this case, the stability does not depend on electrostatic repulsions but on the presence of a layer of water solvation molecules. These molecules are linked to silanol groups which cover the particle surface. The sol is then lyophilic. In the intermediate pH range, the solvation effect decreases and the electrostatic repulsions forces are too weak to prevent fast and strong aggregation of the particles by means of silanol condensation. Above pH 10, silica dissolution involves more complex phenomena. Another point of interest concerns the silica sol rheology. The viscosity of oxide dispersions generally decreases with increase of the zeta potential,² and repulsion forces hinder particle aggregation. For silica sols, Greenberg *et al.*³ have shown an opposite effect. The viscosity passes through a maximum for pH 10. Recently, Tarasevich *et al.*⁴ have underlined the influence of pH on particle packing after electrolytic destabilisation and centrifugation of the silica sol. A less dense packing is obtained for pH values of ~ 10 . These results differ from those obtained by sedimentation of larger particles (0.1–1 μm in diameter) for oxides such as TiO₂,⁵ Al₂O₃⁶ and also SiO₂.⁷ Two phenomena seem to be responsible for this behaviour of silica sols: the peculiar mechanisms of stabilisation and the colloidal character of the particles (which are only a few nanometers in diameter). The aim of this work is to improve understanding of the behaviour of these silica sols. The evolution of the sol viscosity is studied as a function of the volume fraction of the dispersed phase for various pH values. Quasi-elastic light scattering (QLS) measurements are used to determine the hydrodynamic radius of the particles in dilute sols. These values are compared with those deduced from viscometric measurements.

2 Experimental Procedure

2.1 Materials

The starting material is a commercial silica sol (Syton 30 X-Monsanto). Its SiO₂ content is 30 wt%. The stabilizing counter-ion is Na⁺. The free sodium content is 0.3 wt%, expressed as Na₂O. The sol's density at 15.5°C is 1.20–1.21. Its pH at 20°C ranges from 9.6 to 10, the measured value at 25°C usually being 9.7.

The specific surface area of the dried material measured by nitrogen adsorption according to the BET method is $156 \times 10^3 \text{ m}^2/\text{kg}$. In our case, this value is found to be nearly constant, not depending on the method of sol destabilization, and by way of consequence on the texture of the gel. Thus, the area of contact between aggregated particles (necks) can be assumed to be negligible compared with the area of the particles themselves, as measured by adsorption–desorption isotherms of nitrogen molecules. The equivalent spherical radius of the silica particles, r_{seq} , can then be obtained using the following relation:

$$r_{\text{seq}} = \frac{3}{S_{\text{sp}} \rho_s} \quad (1)$$

where S_{sp} is the measured specific surface area and ρ_s is the density of amorphous silica ($\sim 2.2 \times 10^3 \text{ kg/m}^3$).

The equivalent spherical radius for this sol is 87–88 Å. It should be noted that the particle radius calculated from specific surface area is usually lower than that evaluated by means of electron microscopy observations.⁸ This phenomenon can be explained by the existence of a very low percentage of fine particles which are not taken into account using electron microscopy or by a possible roughness of the particle surface.¹

The following procedure is used to dilute the sol and to maintain its pH at a given value. The sol is first diluted in distilled water at a concentration slightly higher than the final one. The suitable pH value is then obtained by adding dropwise a dilute solution of sodium hydroxide (pH 11) or nitric acid (pH 2, 4, 6 and 8). The suitable dilution is finally reached by addition of water previously maintained at the desired pH value with sodium hydroxide or nitric acid (Table 1). For pH 9.7, the sol is directly diluted with distilled water maintained at pH 9.7 using sodium hydroxide (Table 1). The investigated concentrations correspond to volume fractions of the solid phase (silica), Φ_s , of 0.1227, 0.0818, 0.0409, 0.01636 and 0.00818.

Table 1. Amounts of electrolytes in the dilute sols

	pH 2	pH 9.7	pH 11	Na ⁺ from starting sol
The most concentrated sol ($\Phi_s = 0.1227$)	10^{-1}	5×10^{-4}	10^{-1}	9×10^{-2}
The most dilute sol ($\Phi_s = 0.00818$)	10^{-2}	10^{-3}	10^{-2}	6×10^{-3}

HNO₃ (pH 2) or NaOH (pH 9.7 and 11) was added for dilution and pH adjustment of the sols (expressed in mole per liter of dilute sol).

Free Na⁺ ions were introduced with the starting sol (expressed in atom gram per liter of dilute sol).

2.2 Measurements

2.2.1 Viscometry

The sol viscosity η_D is determined using a capillary flow viscometer, at 25°C. This equipment allows automatic recording (using two photoelectric cells) of the time t necessary for a given amount of sol to flow through a capillary tube. The capillary tube is an Ubbelohde tube (dia. 0.5 mm) working with a temperature-regulated jacket. If ρ is the density of the sol, we can write

$$\frac{\eta_D}{\rho} = At \quad (2)$$

A is a constant value related to the geometrical features of the viscometer. It is previously determined using standard liquids.

The density of the sol at 25°C is measured using a densimeter. The sample cell is a hollow diapason. The resonance frequency ν is a function of the sol density:

$$\rho = A'/\nu^2 + A'' \quad (3)$$

where A' and A'' are constant values determined using standard liquids.

2.2.2 Quasi-elastic light scattering

This technique, also called photon correlation spectroscopy, allows the measurement of diffusion coefficient D of the particles in the sol. For very dilute dispersions, there is no interaction between colloidal particles, and the Stokes-Einstein relation applies:

$$D = \frac{kT}{6\pi\eta_0 r_H} \quad (4)$$

where k is the Boltzmann constant, T is the temperature and η_0 is the solvent viscosity.

The hydrodynamic radius of the particles, r_H , can be determined from eqn (4).

In the case of polydispersed suspensions, the cumulant method (fit procedure) can be used to evaluate a mean hydrodynamic radius r_H .⁹

The diffusion coefficient of particles in concentrated dispersions differs strongly from the value found with infinitely dilute medium.¹⁰ Moreover, the diffusion coefficient of charged particles can be reduced by several per cent if the double layer thickness is comparable to the particle radius.¹¹

The measurements are performed at 25°C with an argon laser source ($\lambda = 5145 \text{ \AA}$). The homodyne mode is used. The scattered light for a given angle is detected by a photomultiplier. A correlator performs the real-time calculation of the correlation function of the photocurrent, which is proportional to the correlation function of the scattered intensity. The sample time and the accumulation duration are respectively 1.5–3 μs and 100 s. A computer determines the decay rate of the correlation function, from which is deduced the translational collective diffusion coefficient D . At a given pH value, the two most dilute sols ($\Phi_s = 0.01636$ and 0.00818) are analyzed for two angles, 90 and 140°.

The best treatment of the experimental data is obtained with a one-cumulant method. This fact suggests that the studied sols are not strictly monodispersed sols but consist of particles with a relatively sharp size distribution. This is a usual characteristic for this type of silica sols, whose particles have mainly a spherical shape.

3 Results and Discussion

3.1 Viscometric data

The results of viscosity measurements are reported in Fig. 1. The relative viscosity η_r (ratio of the

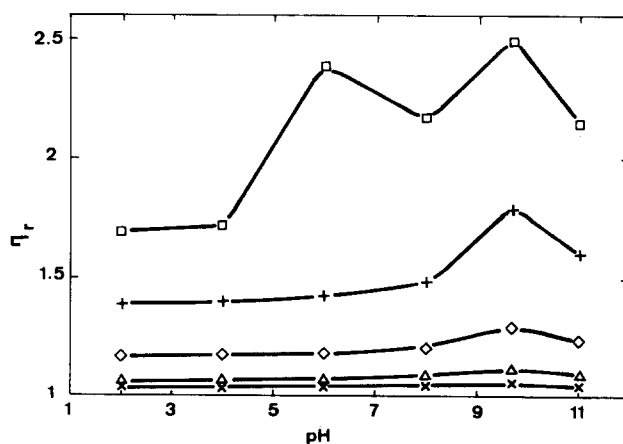


Fig. 1. Relative viscosity η_r of sols versus pH for various volume fractions of solid phase Φ_s : □, 0.1227; +, 0.0818; ◇, 0.0409; △, 0.01636; ×, 0.00818.

viscosity of the dispersion η_D to that of the solvent, η_0) shows a variation identical to that previously described by Greenberg *et al.*³ The upper relative viscosity is obtained at pH 9.7. The higher the silica concentration of the sol, the more pronounced is this phenomenon. The curve corresponding to the highest silica concentration exhibits a second maximum at pH 6. In the pH range 6–8, the rapid gelation process (gelation time of a few hours) induces an increase of viscosity related to particle aggregation. This phenomenon, which modifies the viscosity values, is not observed in the most dilute solutions.

3.2 Remarks on the evolution of viscosity as a function of the volume fraction of dispersed phase

Einstein¹² published a theoretical analysis of the viscosity of dilute solutions, and gave a relation describing the evolution of the viscosity of a dilute dispersion of hard spheres as a function of the volume fraction of the spheres, Φ_D .

The relative viscosity, η_r , is expressed by

$$\eta_r = \eta_D/\eta_0 = 1 + 2.5\Phi_D \quad (5)$$

However, this expression is valid for a volume fraction of the dispersed phase of only a few per cent. The Einstein equation does not take into account hydrodynamic interactions. When the volume fraction of the dispersed phase increases, the viscosity increases more rapidly than predicted by this equation. Many studies have been made of the viscosity evolution of dispersions which have higher volume fractions of dispersed phase.^{13–17} More complex expressions have been proposed to evaluate the viscosity η_r for values of Φ_D as high as several tens per cent. The agreement with the experimental data is usually good up to $\sim 25\%$. Above this value,

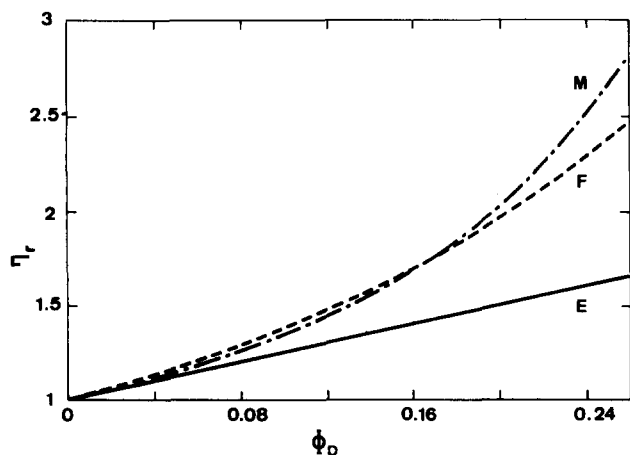


Fig. 2. Variation of the relative viscosity η_r as a function of the volume fraction of dispersed phase Φ_D according to the following relations: Einstein (E), Mooney (M) and Farris (F).

marked discrepancies between theoretical curves and experimental values can be observed. On the other hand, the particle size distribution has to be considered.¹⁵ Figure 2 shows the evolution of η_r versus Φ_D according to two simple expressions, established by Mooney¹³ and Farris.¹⁵ In the volume fraction range 0–0.25 the difference between the two curves is not significant.

The first relationship is¹³

$$\eta_r = \exp\left(\frac{2.5\Phi_D}{1 - k\Phi_D}\right) \quad (6)$$

where k is a constant value, named the self-crowding factor. The experimental data are correctly described with a value for k of 1.43.¹³

The second expression is¹⁵

$$\text{for } \Phi_D < 0.25, \quad \eta_r = (1 - \Phi_D)^{-K} \quad (7)$$

It was demonstrated¹⁵ that a K value close to three describes most of experimental data.

3.3 Analysis of the curves of viscosity versus silica concentration

The evolution of the relative viscosity of sols versus their volume fraction of solid phase (silica) Φ_S is shown in Fig. 3. The curves corresponding to expressions (6) and (7) are also shown. Large differences appear between the experimental and theoretical curves. Moreover, the relative viscosity strongly depends on the pH for a given Φ_S . These facts suggest that the volume fraction of the solid phase is not the correct parameter to describe the evolution of the relative viscosity. The dispersed phase does not consist only of the solid phase.

The small size of the colloidal particles has to be taken into account. A layer of chemical species is

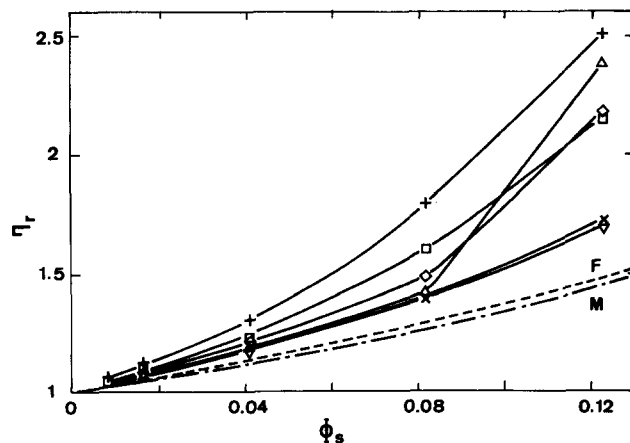


Fig. 3. Relative viscosity η_r of sols as a function of the volume fraction of solid phase Φ_S at various pH: ∇ , pH 2; \times , pH 4; Δ , pH 6; \diamond , pH 8; $+$, pH 9.7; \square , pH 11. Theoretical curves are according to the relation of Mooney (M) and Farris (F).

adsorbed on the surface of a particle, and follows the particle during its motion. This increases the volume fraction of the dispersed phase. For silica, the adsorption phenomenon is influenced by the pH. For pH values of ~ 10 , an electric double layer is formed by adsorbed ionic species. The ions of the inner part of the double layer are strongly bonded to the particle. It is known that the shear plane which corresponds to a rapid change of viscosity is situated beyond the external boundary of the inner part of the double layer. As the pH decreases, the surface ionization of silica particles decreases. Near the isoelectric point (pH ~ 2), weak ionization of the surface silanol groups allows adsorption of water molecules by hydrogen bonding.

These suspensions can be better described using a new radius for the colloidal particles. This radius, named the hydrodynamic radius r_H , takes into account the layer of adsorbed species. Its value can be determined from viscometric data. For a given sol of volume fraction of solid phase Φ_S , the volume fraction of dispersed phase Φ_D is calculated from the experimental value of η_r and a theoretical expression such as relation (6) or (7). The hydrodynamic radius r_H is then determined according to the following relation:

$$\frac{\Phi_D}{\Phi_S} = \left(\frac{r_H}{r_S}\right)^3 \quad (8)$$

where r_S is the radius of the solid particle (silica).

We consider a sol with a volume fraction of solid phase $\Phi_S = 0.0818$ for each studied pH value. For this silica concentration any aggregation phenomenon occurs during the viscometric measurements. r_H is calculated using $r_S = 88 \text{ \AA}$ (Fig. 4).

For the other silica concentrations the volume fractions of the dispersed phase are calculated assuming that Φ_D/Φ_S is constant. This hypothesis

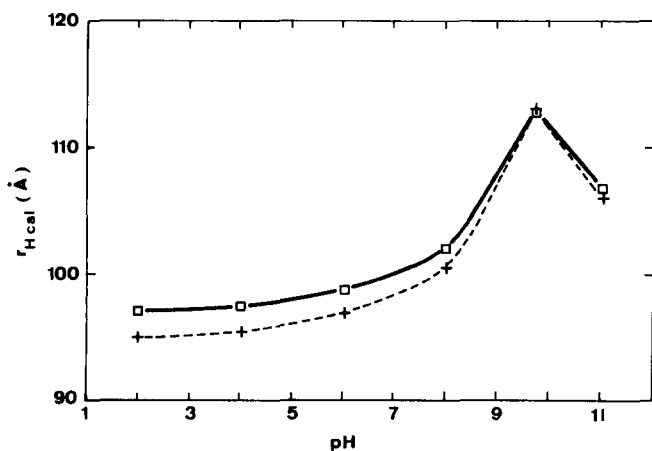


Fig. 4. r_H calculated from both viscometric data and relation of Mooney (\square) or Farris ($+$) versus pH.

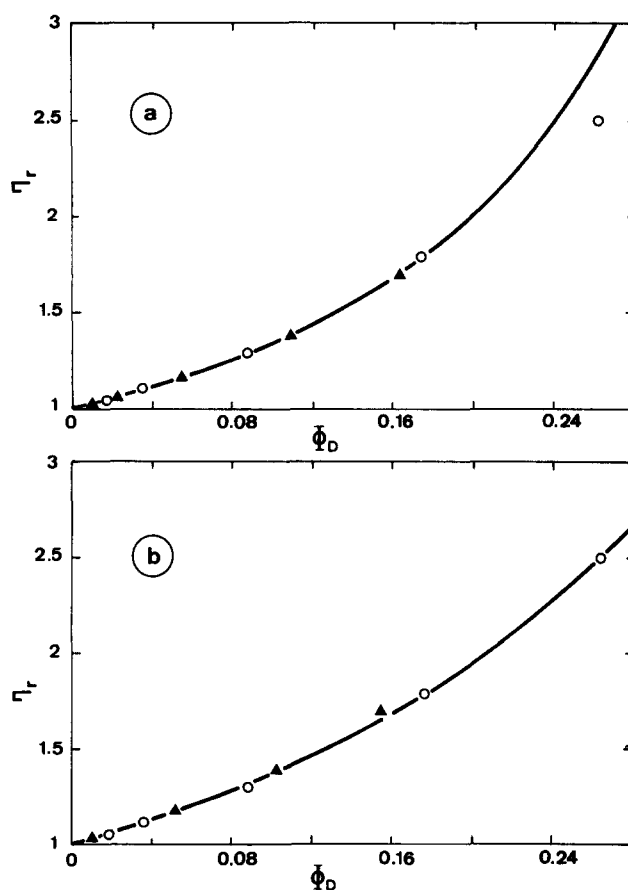


Fig. 5. Relative viscosity η_r for sols (\blacktriangle , pH 2, \circ , pH 9.7) as a function of Φ_D calculated using the relation of Mooney (a) and Farris (b). (The solid lines are the theoretical curves.)

implies that the hydrodynamic radius r_H is not modified by dilution or concentration of the sol. There is no strong discrepancy between the curves of η_r as a function of the computed value Φ_D and the theoretical curves of the Mooney or Farris expressions (Fig. 5). This agreement is significant only for high volume fraction of dispersed phase, when the viscosity of the dispersion is sensitive to weak variations of Φ_D . It can be deduced that r_H does not vary strongly with the concentration of the sol for the highest silica concentrations.

3.4 Sols maintained at pH 9.7

At pH 9.7, r_H is in the range 110–115 Å. This value defines a surface layer of 20–25 Å in thickness according to the expected value for this type of sol.¹ This layer does not correspond to the inner part of the electric double layer but probably to the whole double layer.

It is clear that the presence of this surface layer plays an important role in gelation when the colloidal particles are brought together, and consequently has an effect on the texture of the wet and dried gels. To understand this phenomenon we can assume two simplifying hypotheses:

- (1) The surface layer of the particle is not modified during concentration of the sol until the gel point.
- (2) At the gel point we assume that the monodispersed particles surrounded by their adsorbed layer pack in the densest arrangement (volume fraction 0.74).

At pH 9.7, the value of r_H is 115 Å (Fig. 4). Thus the volume fraction of solid phase in the wet gel should be only ~33%. During the drying treatment the surface layer must disappear. Even with this arrangement a large shrinkage is then expected. This shrinkage will favor cracking of the gel during this step.

Keeping r_H constant and considering now a random close packing of spheres (volume fraction ~0.64), the volume fraction of solid phase in the wet gel should be 29%. This value is comparable with the value of 22% obtained by Tarasevich *et al.*⁴

3.5 Sols maintained at pH 2

The calculated hydrodynamic radius decreases strongly for pH values below 9.7 (Fig. 4). Moreover, a less dense packing is expected for these sols, which show a lower resistance to aggregation. However, the lower ratio Φ_D/Φ_S will involve smaller shrinkage during the gel drying.

At pH 2, the thickness of the adsorbed layer is in the range 6–10 Å, which corresponds to two or three molecular layers of adsorbed water. This value is intermediate between the value determined by Iler and Dalton¹⁸—a monolayer for a sol maintained at pH 2—and the value determined by Greenberg *et al.*¹⁹—five or six layers for a sol maintained at pH 2.8. It is noteworthy that the conditions and calculation procedure are slightly different for each case. Iler and Dalton¹⁸ calculated the layer number directly, using a value of the volume fraction of the dispersed phase determined by means of Mooney's relation. The viscosity measurements were performed on sols with a solid phase volume fraction of 0.017 or 0.030. To determine the thickness of the adsorbed layer h , Greenberg *et al.*¹⁹ used the expression

$$\frac{b}{2.5} = \left(\frac{r_s + h}{r_s} \right)^3 \quad (9)$$

where b is the slope of the straight line which describes the evolution of the specific viscosity of the dispersion, $\eta_s = \eta_r - 1$, as a function of Φ_s . This procedure is equivalent to ours but makes use of Einstein's relation ($\eta_s = 2.5\Phi_D = b\Phi_s$). b was obtained from viscosity measurements of dilute sols

($\Phi_s \leq 0.014$). The large number of molecular layers determined using viscometry could explain the unusually large molecular weights obtained from light scattering experiments as compared with that expected from the size of the dried particles.³

A volume fraction of solid of ~52.5% was obtained at pH 2.⁴ In that case, the expected total shrinkage with respect to the full densification of the gel will also be strongly reduced. The average coordination number of the particles, n , can be evaluated according to the equation²⁰

$$n = 2 \exp(2.4\Phi) \quad (10)$$

where Φ is the volume fraction occupied by the particles.

Assuming no adsorbed layer ($\Phi = \Phi_s$), n takes its minimum value of seven. A high value of n could be explained by sinking of the gel network under the effect of the centrifugation which was used. However, Iler¹ indicated that high colloidal silica concentrations can be obtained maintaining pH 2. Using a mixture of particles of different sizes it is possible to produce dried material which has a volume fraction of solid close to 80%. The dense packing obtained in this pH range may be related to the existence of short-range repulsive interactions. These interactions are due to solvation of the particles, which prevents aggregation.

3.6 Quasi-elastic light scattering measurements of the hydrodynamic radius

As mentioned above, highly dilute sols must be used to carry out a correct measurement of r_H by QLS. The values determined at two different angles (90 and 140°) for sols with $\Phi_s = 0.00818$ and 0.01636 are similar (differences of only a few ångströms). The average values are shown in Fig. 6. A maximum is observed at pH 9.7. At this pH, the obtained value of

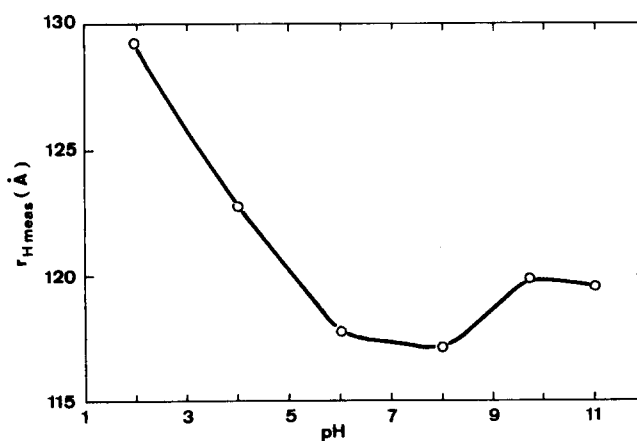


Fig. 6. r_H measured using QLS versus pH.

r_H (120 Å) for a dilute sol corresponds to that obtained from viscometric measurements performed on more concentrated sols (115 Å). Below pH 8, the measured hydrodynamic radius increases as the pH decreases, and marked differences from previous calculations appear (Fig. 4). The highest measured hydrodynamic radius is obtained at pH 2 ($r_{H \text{ meas.}} = 130 \text{ Å}$), whereas the calculated value is 94–98 Å. This difference can be explained by the presence of a thick water layer on the surface of silica particles in the dilute sols used for QLS measurements. For higher silica concentrations the particle interactions involve shear stresses on this layer, which is destroyed. The number of molecular layers thus decreases.

To explain the variation of r_H versus pH and dilution we have also considered the effect of the ionic strength of the colloidal solution. In the electrical double layer theory the diffuse layer 'thickness' or Debye-Hückel length is directly related to the ionic strength of the dispersion.²¹ This approach does not agree with our results except for the sols at pH 2. However, in that case, the double layer concept is not suitable to describe the behaviour of a dispersion with a 'lyophilic' character.

4 Conclusion

Viscometric measurements are performed on a silica hydrosol maintained at various pHs. They show clearly that the evolution of the viscosity as a function of the volume fraction of the dispersed phase cannot be described by the classical expressions of viscosity if the dispersed phase is calculated from the solid phase. Considering the presence of an adsorbed water layer on the particles, it is possible to relate η_r to Φ_D using classical equations. The hydrodynamic radius of a stable sol maintained at pH 9.7 evaluated from viscometric measurements is of the same order of magnitude as the value measured using QLS. However, it is larger than the real radius of the solid particle (there is a difference of 20–30 Å). This fact can explain the low volume fraction of solid phase observed for these stable sols, which produce gels with a close-packed arrangement of colloidal particles. At low pH, a discrepancy is observed between the value of r_H measured using QLS and the value deduced from viscometric data. This difference may be related to the presence of several molecular layers of adsorbed water at high dilution. Most of these layers disappear when the sol becomes concentrated.

It must be noted that other colloidal dispersions, such as, for instance, boehmite sols, have a different behaviour. The stabilisation mechanism of these alumina sols differs from that of the silica sols (for more details see Ref. 22). The more stable and less viscous sols present a lower relative volume of gel for gelation by evaporation of the liquid phase.^{23,24}

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