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Intrinsic viscosity of SiO_2, Al_2O_3 and TiO_2 aqueous suspensions

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Abstract

The viscosity of dilute suspensions of several metal oxides (SiO_2, Al_2O_3 and TiO_2) was measured at different pH values. The intrinsic viscosity, $[\eta]$, was derived from the concentration dependence of the viscosity. This magnitude was pH-dependent. A correlation with the shape of the kinetic unity has been proposed.

Keywords: Intrinsic viscosity; Suspensions; Oxides; Colloids; Electroviscous effects

1. Introduction

Experimentally it has been found that the viscosity of a very dilute colloidal suspension is linearly dependent on the solid volume fraction [1–4]. The viscosity of a dilute suspension is higher than that of the fluid phase due to two main contributions. Firstly, the presence of the particles distorts the flow field, which gives place to an increase in the dissipation of energy. Secondly, the distortion of the electrical double layer that surrounds the particles supposes an additional dissipation energy [5]. An expression that groups both effects was proposed time ago [6],

$$\eta = \eta_0\big(1 + [\eta](1 + p)\phi\big). \tag{1}$$

In this equation η is the viscosity of the suspension, η_0 the viscosity of the liquid phase, $[\eta]$ the intrinsic viscosity, p the primary electroviscous coefficient, and ϕ is the solid volume fraction in the suspension. The primary electroviscous coefficient mainly depends on the electrical state at the solid–liquid interface, and the intrinsic viscosity is mainly determined by the geometry of the suspended particles. For example, Einstein [7] obtained, from theoretical considerations, that $[\eta] = 2.5$ for spherical particles. For other particle shapes, it is obtained $[\eta] > 2.5$ [6].

Generally, it has been accepted that the electrical state of the solid–liquid interface has no influence on the value of the $[\eta]$ parameter. However, the variation of the inter-particle interactions due to, for example, the decrease of its repulsive electrical energy, such as it is established by the DLVO theory [8,9], gives place to the formation of aggregates (clusters) of particles. Then the kinetic unity is a cluster of particles instead of a single particle, and the $[\eta]$ parameter should consequently change. This argument was used time ago [10], but in that case was the shear rate the magnitude of which promoted the formation of clusters. In this paper we will determine the influence of the variation of the repulsive energy between particles on the intrinsic viscosity of several oxide suspensions.

The paper is organised as follows: In the following section the experimental setup is described and in Section 3 the experimental results are discussed.

2. Experimental

The titanium oxide (anatase) was supplied as a white powder by Aldrich. The material (purity of 99.9%) was used without any further purification. As pointed out by Gustafsson et al. [11], attempts to further purification of the powder led to contamination. Electron microscopy (JEOL JSM840 scanning microscope) showed that the particles are roughly spherical with a mean diameter of 200 ± 10 nm. The apparent specific surface area$_{BET}$ of these particles was determined by N_2 ad-

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Table 1
Physical and chemical properties of the suspensions

Material	Shape	Size (nm)	$Area_{BET}$ (m^2/g)	pH_{IEP}
SiO_2	Spherical	7 ± 2	390	4.3
Al_2O_3	Irregular	100 ± 10	142	9.1
TiO_2	Spherical	200 ± 10	10	3.5

sorption at 77 K by using an Autosorb-1 (Quanta Chrome) apparatus, the result being 10 m^2/g.

The alumina used here was γ-Al_2O_3 manufactured by the Goodfellow Cambridge Ltd. (England). This material is presented as a powder with a purity of 99.995%. In order to remove soluble salts and other impurities, the alumina was dialysed in deionised water for 7 days, with the deionised water being changed at the beginning and end of each day [12]. Thereafter, the alumina suspension underwent sedimentation for 24 h. The suspension thus obtained was filtered through a filter with a pore size of 0.1 μm and dried in order to store it in dry form to avoid contamination from trace impurities from electrolytes or water and soluble silicate. The shape and morphology of the alumina particles were determined by electron microscopy. The images showed that the particles are highly ordered crystalline grains with distinct planar faces and irregular forms. The apparent specific surface $area_{BET}$ of these particles was 142 m^2/g.

Silica fumed (Sigma–Aldrich) was used in this work as was supplied by the manufacturer. The purity of this powder was 99.8%. The primary particles are spherical with a diameter 7 ± 2 nm. The apparent specific surface $area_{BET}$ of these particles was 390 m^2/g.

The IEP is defined as the pH value in which the electrokinetic or ζ-potential takes zero value. The determination of this parameter was accomplished by measuring the electrophoretic mobility of the suspensions, and converting this magnitude to ζ-potential with Ohshima equation [13]. The results corresponding to the oxides here studied are shown in Figs. 1a–1c. As can be seen in Table 1, the IEP is basic for alumina and acidic for anatase and silica. Other properties of the particles have been summarised in the same Table 1.

All chemicals were of A.R. quality. The water was purified by reverse osmosis followed by percolation through charcoal and mixed bed ion exchange resins (Millipore).

The ζ-potentials were calculated from electrophoretic mobility data. The electrophoretic mobilities were measured with a Zetasizer 2000 (Malvern Instruments) by taking the average of at least six measurements at the stationary level in a rectangular cell.

The viscosity of the suspensions was determined with an Ubbelohde-type (Schött-Gerate) capillary viscometer for dilution, and a rheometer Rheostress RS600 (Haake). The capillary viscometer was calibrated using deionised water at 20, 25 and 40 °C for the determination of the constants of the apparatus. The average maximum shear rate of the viscometers was 230 s^{-1}. Starting from a fixed volume (15 ml) of the initial sample, the volume fraction of the particles was varied by diluting in 5 ml steps with the same liquid phase present in the suspension. In the case of suspensions with a fixed pH, initial and final pH values of the suspensions were measured and the mean value was taken. Although a dependence of the pH on the volume fraction exists, which results from the adsorption of potential-determining ions onto the surface of the particles, it was not appreciable at these low ϕ variations, the deviation between initial and final pH values being less than 1%. As the effect of the presence of the particles on the suspension viscosity

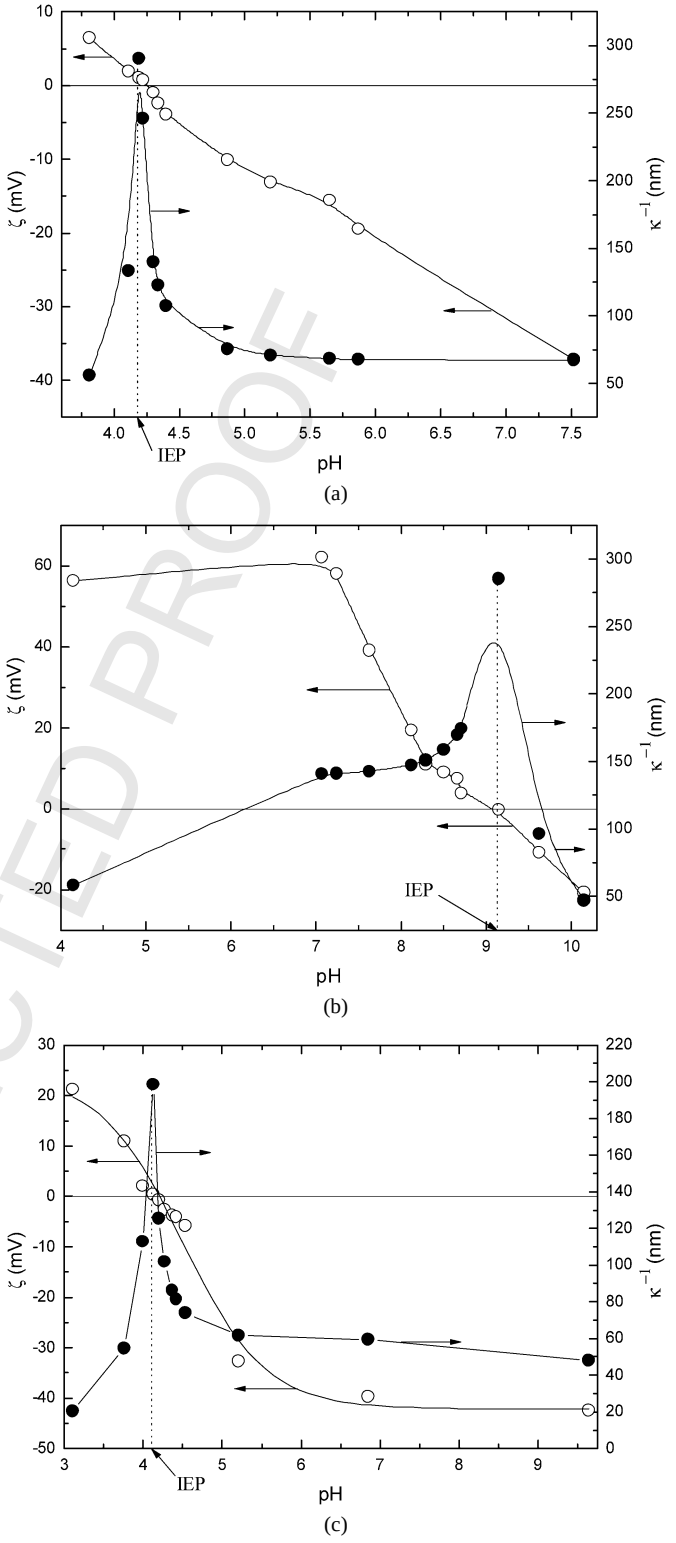

Fig. 1. ζ-potential and κ^{-1} values of the suspensions of different oxides vs pH. (a) SiO_2, (b) Al_2O_3 and (c) TiO_2.

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is low, the uncertainties associated with the manual determination of the efflux time in the viscometers may easily mask the actual viscosity variations. For this reason we have used an automatic system for recording the time (AVS310, Schött-Gerate). Strong sonication was given to the samples before measuring (at least 30 min sonication was necessary for silica in order to obtain reproducible results). After each dilution the suspension was stirred with a magnetic stirring rod, before a new measurement of the efflux time was started. The measurements with the rheometer RS600 were performed in control stress mode. Cone–plate geometry was used. The diameter of the titanium cone and plate was 60 mm, and the angle of the cone was 1°.

The pH of the suspensions was measured with a pH-meter (GLP22, Crison) by using a special probe for "difficult" samples (52-21, Crison).

To obtain the dynamic viscosity of a suspension it is necessary to know its density. This magnitude was obtained with a DMA-58 densimeter (Anton Paar).

All experiments were performed at 25 °C.

3. Results and discussion

The viscosity of a very dilute hard particles suspension, η, is greater than that of the solvent, η_0. This effect was theoretically predicted by Einstein [7] and it is expressed as

$$\eta = \eta_0\big(1 + [\eta]\phi\big). \tag{2}$$

In this equation $[\eta]$ is the intrinsic viscosity, which takes the value 2.5 for spherical and uncharged particles and higher values when this geometric condition is not accomplished [6]. ϕ is the volume fraction of solid particles in the suspension. The validity of Eq. (2) is limited to an extremely diluted suspension of uncharged particles. If one of these two conditions is not accomplished, this equation must be modified.

Several expressions [14–19] have been proposed to express the effect of an increase of the solid volume fraction on the viscosity of a hard particles suspension. However a power series in ϕ, that takes into account the particle–particle interactions at several orders, was shown valid for the discussion of the experimental results [18],

$$\eta = \eta_0\big(1 + [\eta]\phi + K[\eta]^2\phi^2 + O(\phi^3) + \cdots\big), \tag{3}$$

where K is the Huggins coefficient.

Von Smoluchowski [6] proposed an expression that takes into account the resistance of ionic atmosphere (the electrical double layer) that surrounds the particles against fluid distortion of shear. This is known as the primary electroviscous effect. Equation (1) is Smoluchowski's result, now $[\eta](1 + p)$ being the intrinsic viscosity of the colloidal suspension. Following Adachi et al. [20], we can distinguish between the intrinsic viscosity when the electrical effects are not manifested (hard particles), and that when the electroviscous effects are present. They are related as

$$[\eta]_{\mathrm{EEV}} = [\eta](1 + p). \tag{4}$$

The primary electroviscous coefficient, p, was obtained by Booth [21] for arbitrary double layer thickness but limited to small surface potentials,

$$p = q^*\left(\frac{e\zeta}{kT}\right)^2 Z(\kappa a)(1 + \kappa a)^2. \tag{5}$$

Here, e is the proton charge, ζ the zeta or electrokinetic potential, k the Boltzmann's constant, T the absolute temperature, and $Z(\kappa a)$ the relaxation function given by Booth [21]. The electrokinetic radius, κa, is the ratio of the particle radius a to the screening Debye length,

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon kT}{\sum_{i=1}^{N} z_i^2 e^2 n_i}}, \tag{6}$$

where ε is the permittivity of the liquid medium and n_i and z_i are the numeric concentrations and the valences, respectively, of the N ionic species in the solution, far away from any particle. Finally, the term q^* is given by

$$q^* = \frac{6\varepsilon kT}{e\eta_0}\frac{\sum_{i=1}^{N} n_i z_i^2/\omega_i}{\sum_{i=1}^{N} n_i z_i^2}, \tag{7}$$

where ω_i is the mobility of the i-type ion. The calculation of the sums is not evident. A controversy on the actual electrolyte concentration in a colloidal suspension has grown in colloid discussions. The idea of ion condensation near the surface particle due to its surface charge has now been considered. In line with this model, a hypothesis on the electrical double layer ion concentration was established elsewhere [22]. It is supposed that the surface charge is entirely screened or neutralised at the IEP, and there is no EDL that surrounds the particles at this pH value. The basic idea that supports this hypothesis is that at the IEP the continuum is a saturated system of ions with the same distribution at the particle surface than into the bulk. The colloidal particles are immersed into this continuum. Therefore, at the IEP the liquid phase of the suspension will be considered as the blank reference. Consequently, when $\mathrm{pH} \neq \mathrm{pH_{IEP}}$, the differences $\Delta\mathrm{pH} = \mathrm{pH} - \mathrm{pH_{IEP}}$ and $\Delta\mathrm{pOH} = \mathrm{pOH} - \mathrm{pOH_{IEP}}$, together with the background electrolyte concentration, will determine the charge in the EDL (Fig. 2). Taking into account this hypothesis on the ion concentration in the EDL, Booth's coefficient takes the form:

$$p = \frac{6e\varepsilon\varsigma^2}{\eta_0 kT} Z(\kappa a)(1 + \kappa a)^2 \times \left[\frac{\frac{|10^{-\mathrm{pH}} - 10^{-\mathrm{pH_{IEP}}}|}{\omega_{\mathrm{H}}} + \frac{|10^{-\mathrm{pOH}} - 10^{-\mathrm{pOH_{IEP}}}|}{\omega_{\mathrm{OH}}} + \frac{C_{\mathrm{M}}}{\omega_{\mathrm{M}}}}{|10^{-\mathrm{pH}} - 10^{-\mathrm{pH_{IEP}}}| + |10^{-\mathrm{pOH}} - 10^{-\mathrm{pOH_{IEP}}}| + C_{\mathrm{M}}}\right] \tag{8}$$

and the screening Debye length,

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon kT}{e^2 N_{\mathrm{A}} 10^3 [C_{\mathrm{M}} + |10^{-\mathrm{pH}} - 10^{-\mathrm{pH_{IEP}}}| + |10^{-\mathrm{pOH}} - 10^{-\mathrm{pOH_{IEP}}}|]}}, \tag{9}$$

where C_{M} is the molar concentration of the counter-ion added to the suspension and N_{A} is the Avogadro number.

It is worthy to emphasise that, in these models on the viscosity of suspensions, the effect of the agglomeration of particles is not taken into account. A completely dispersed suspension is

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assumed in all cases. However, it is well known that clusters are formed in the particle suspensions. Depending on the particle–particle and the particle–liquid phase interactions, the shape and size of the clusters will vary. We can accept that the difference with respect to a suspension of single particles is the size and the shape of the new entities that can move through the liquid phase when a flow field is established. Really, the existence of this particle structure gives place to non-Newtonian behaviours (shear-thinning, shear-thickening, thixotropy, viscoelasticity), but only at high or moderate particle concentrations. Because we have studied very dilute suspensions, these non-Newtonian effects have not been observed.

The viscosity of SiO_2, Al_2O_3 and TiO_2 suspensions, at different pH and solid volume fractions, has been measured. In Fig. 3, the inherent viscosity is plotted against the volume fraction of silica particles. As can be seen in this figure, the electroviscous effects appeared more clearly for the systems far from the isoelectric point, where the electrical double layers are thicker (Fig. 1a). That is, when the pH is more different from the IEP, the intrinsic viscosity which is the intercept of the extrapolation of the plot at $\phi = 0$ will increase, and the slope of the curve, which reflects the presence of second order effects, also increase. In Fig. 4, the inherent viscosity of aqueous alumina suspensions is plotted against the solid volume fraction. Again, the electroviscous effects are more evident in systems far from the IEP, where κ decreases and ζ increases (Fig. 1b). However, in this case, only primary electroviscous effect has been observed, as can be deduced from the zero slopes of the curves. The effect of double layer interaction is negligible in these very dilute suspensions ($\phi \leqslant 0.5\%$). From the extrapolation of the plot at $\phi = 0$, the $[\eta]_{EEV}$ values have been obtained. Finally, in Fig. 5, the specific viscosity of aqueous anatase suspensions has been plotted against the solid volume fraction, this last magnitude being less than 1%. The results suggest, like with alumina suspensions, that only primary electroviscous effect is present in these systems. Again, the electrical double layer thickness increases the higher is the difference between the pH of the suspension and the IEP (Fig. 1c). The intrinsic viscosity when the primary electroviscous effect is present is obtained from these experimental results. In all cases, a correlation between the electrical double layer thickness, the ζ-potential values and the intrinsic viscosity of the suspensions have been obtained.

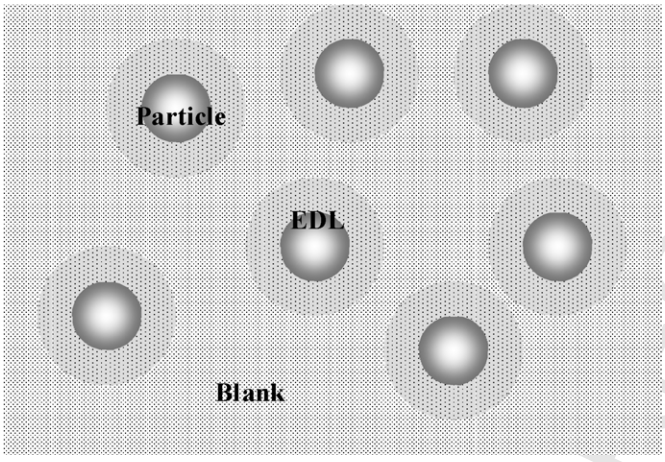

Fig. 2. The hypothesis on the electrical double layer ion concentration.

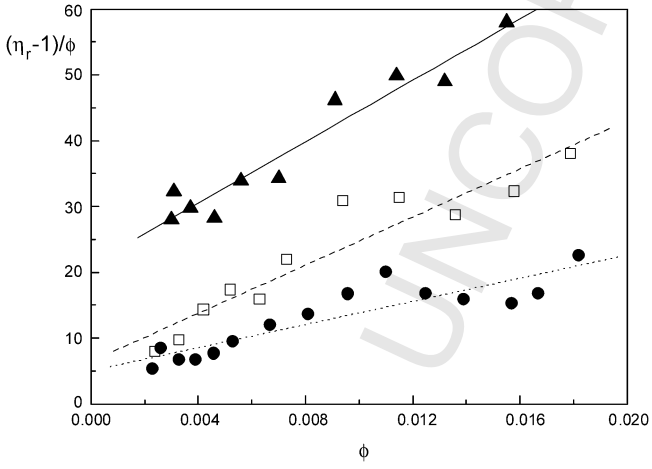

Fig. 3. Inherent viscosity of SiO_2 suspensions at different pH values: (▲) pH 6.1, (□) pH 2.6, (●) pH 4.9.

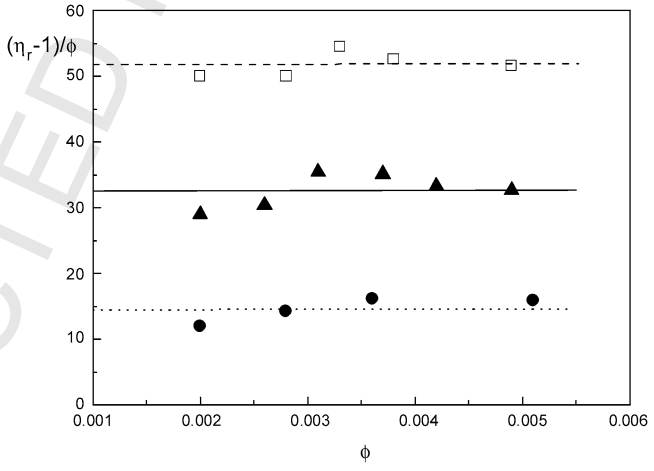

Fig. 4. Inherent viscosity of Al_2O_3 suspensions at different pH values: (□) pH 11.4, (▲) pH 6.3, (●) pH 7.9.

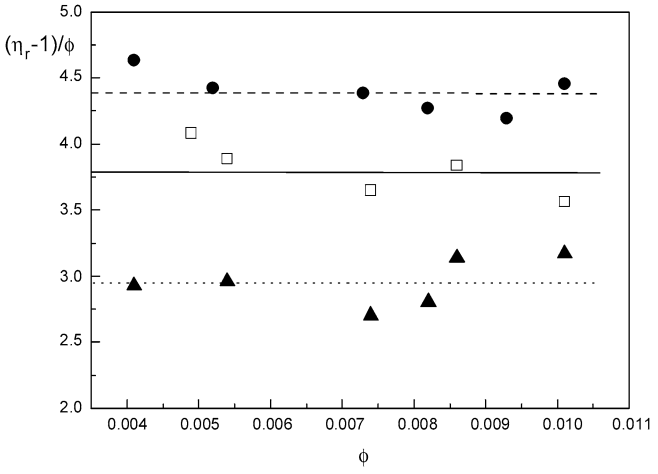

Fig. 5. Inherent viscosity of TiO_2 suspensions at different pH values: (●) pH 5.9, (●) pH 4.7, (▲) pH 4.2.

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Table 2
Booth's primary electroviscous coefficient, the intrinsic viscosity, the axial ratio of the equivalent ellipsoid of revolution, and the particle volume fraction in a cluster

Material	ΔpH	p_{Booth}	$[\eta]$	a/b	ϕ_{pc}
SiO_2	1.8	0.0065	20.9	13.5	0.120
	1.7	0.0022	6.3	5.5	0.397
	0.6	0.0018	5.7	5.0	0.439
Al_2O_3	2.8	0.029	32.1	15.9	0.078
	2.3	0.245	41.8	20.0	0.060
	1.2	0.007	14.9	10.5	0.168
TiO_2	2.4	0.135	3.8	3.2	0.658
	1.2	0.082	3.5	3.0	0.714
	0.7	0.047	2.8	1.2	0.893

The primary electroviscous coefficient has been calculated by using Booth's equation [21]. The validity of Booth's model has been tested [3,22] and it has been assumed in this work. In Table 2 Booth's primary electroviscous coefficient and the intrinsic viscosity, obtained by using Eq. (4) and the experimental $[\eta]_{\text{EEV}}$ values, are shown.

As can be seen, except in one case, the intrinsic viscosity increases when $\Delta\text{pH} = |\text{pH} - \text{pH}_{\text{IEP}}|$ increases. On the other hand, a correlation has been found between the p-value and the intrinsic viscosity. The higher the p-value, the higher the intrinsic viscosity.

The fact that, in absence of electroviscous effects, the intrinsic viscosity was pH-dependent can be explained as follows. The shape of the clusters that may be formed in these suspensions, moving in the flow field, determines the value of the intrinsic viscosity. This magnitude is dependent on the shape of the kinetic unity [23]. Smith and Bruce [10] established a correlation between the intrinsic viscosity and the shear rate applied to suspensions of α-Fe_2O_3 and γ-Fe_2O_3. These authors obtained that the intrinsic viscosity of the suspension decreases with the shear rate. At low shear rates the suspension is more structured forming a network. At high shear rates the shape of the clusters that are formed from the rupture of the network become more and more spherical when the shear rate increases [24]. Therefore the intrinsic viscosity tends to the minimum value when the shear rate increases. In our case, the shape of the clusters is pH-dependent, because the repulsive electrical energy between particles is related to the variation of this parameter. Near the IEP the repulsive force between particles reduces [25], as can be deduced from the ζ-potential and κ values that are shown in Figs. 1a–1c, allowing particles to group in aggregates easily.

Silica particles are spherical, but it is well known that they form aggregates by hydrogen bridges due to the interaction of the silanol groups that form onto its surface. When the electrical repulsive energy is high, far from the IEP, the form of the cluster tends to be a chain. When the electrical repulsive energy is low, near the IEP, the form of the cluster tends to be a sphere. These two last claims are supported by the calculations which were made following Biddle et al. [26]. In this reference a method is proposed to obtain an estimation of the shape and size of particle aggregates. To apply their method it is necessary to combine viscosity and dynamic scattering light measurements (or other similar methods to measure hydrodynamics characteristics of the system) [27, pp. 327, 335]. Then, the axial ratio of an ellipsoid of revolution which is equivalent to the particle aggregate and the values of its axis are obtained. Although we have not in our laboratory a device which can allow us to make dynamic scattering light measurements, only with the intrinsic viscosity data and Simha's plots [27, pp. 335–336], we can determine the axial ratio of the equivalent ellipsoid. The results are shown in Table 2. As can be seen, this magnitude decreases near the IEP, suggesting a less "prolate" ellipsoid.

Alumina particles have a very irregular shape. Near the IEP, the particles form aggregates with a more spherical shape than an isolated particle, but far of this point they tend to form more elongated clusters, as can be deduced from the axial ratio which was calculated following the method by Biddle et al. [26]. The results are shown in Table 2.

Finally, isolated anatase particles are almost spherical. In this case, a very large variation in the intrinsic viscosity due to the formation of clusters is not expected. This is due to that the clusters will tend to be more and more spherical near the IEP, like the isolated particles. The clusters with a very spherical form do not modify the intrinsic viscosity value, because, as was pointed out by Einstein, $[\eta] = 2.5$ independent of the size of the spherical particle. So both near and far from the IEP the intrinsic viscosity should tend to be 2.5 for the anatase suspensions. The results in the Table 2 show that the deviation from this value is small enough to accept the validity of this argument. Moreover, the axial ratio of the equivalent ellipsoid [26] tends to 1 at the IEP, which confirms this description. It is clear that the clusters have a light elongated form far from the IEP.

It is also interesting to determine the compaction of a cluster. In studies on the structure dependence of rheological behaviours (shear-thinning, shear-thickening, thixotropy, etc.) a determining parameter was shown [24,28–30]. From the intrinsic viscosity values, the volume fraction of particles in a cluster can be obtained using the relation derived by Smith and Bruce [10],

$$[\eta] = \frac{2.5}{\phi_{\text{pc}}}. \tag{10}$$

The particle volume fraction in a cluster, ϕ_{pc}, is the quotient between the volume fraction of particles in the suspension, ϕ, and the volume fraction of clusters ϕ_{c}. It is clear that the higher the intrinsic viscosity of the suspension, the lower the particle volume fraction in a cluster. This is a consistent result with the formation of chains of particles far from the IEP: obviously, in these clusters, ϕ_{pc} should be lower than for the more spherical clusters that form near the IEP.

Acknowledgments

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