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Journal of the European Ceramic Society 27 (2007) 2209–2215

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Characterization of rheological properties of colloidal zirconia

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Received 25 March 2006; received in revised form 12 July 2006; accepted 21 July 2006
Available online 22 September 2006

Abstract

Dynamic viscosity of aqueous suspensions of nanosized zirconia (ZrO_2) have been studied for the low volume fraction range. The specific surface area of dry powder was determined from the BET method. The zeta potential of zirconia particles as a function of pH was measured by the microelectrophoretic method. The isoelectric point found in this way was 4.7. The particle density in aqueous suspensions was found by the dilution method. The dynamic viscosity of suspensions was measured by using a capillary viscometer that eliminated the sedimentation effects. Experimental data showed that for dilute zirconia suspension, the relative viscosity increased more rapidly with the volume fraction than that the Einstein formula predicts. This allowed one to calculate the specific hydrodynamic volume of particles in the suspensions and their apparent density. It was found that particles forming zirconia suspensions were composed of aggregates having porosity of 40–50%. The size of the primary particles forming these aggregates was 0.2 μm that agrees well with the BET specific surface data. The influence of an anionic polyelectrolyte:polysodium 4-styrenesulfonate (PSS) on zirconia suspension viscosity also was studied. First the PSS viscosity alone was measured as a function of its volume fraction for various ionic strength of the solutions. The data were interpreted in terms of the flexible rod model of the polyelectrolyte. Then, the viscosity of ZrO_2 in PSS solutions of fixed concentration was measured as a function of the concentration of zirconia. It was revealed that the viscosity of the mixtures was proportional to the product of the zirconia and polyelectrolyte viscosities taken separately.

Keyword: ZrO_2; Dispersants; Rheology; Suspensions

1. Introduction

Understanding the rheological behavior of colloid suspensions is important in the analysis and control of the properties of ceramic materials. High quality and reliability of these products can be achieved by using homogeneous suspensions composed of well-dispersed particles. Besides stability of suspensions and lack of aggregation processes, a high fluidity is vital for producing ceramics of complex geometrical shape with a defect-free microstructure after sintering.[1–3] In many technological processes this is achieved by mixing ceramic powders with organic dispersants to obtained better fluidity of the mixture. Organic–inorganic composites have attracted substantial attention because of the potential of combining advanced properties of organic and inorganic components. Formation of composite films based on polyelectrolyte and inorganic nanoparticles has become the subject of extensive experimental work.[4] Many important studies focused on layer by layer deposition, which utilized electrostatic interactions between oppositely charged species. There is a growing interest in the use of composite materials in humidity sensors, batteries, microelectronic devices, magnetic memories, and quantum dot devices. Novel composite materials containing inorganic nanopatrticles embedded in a polyelectrolyte matrix are currently under investigation for catalytic, optical and other applications.

Ceramic particles can be stabilized in aqueous solutions by electrostatic and steric interaction. However, it is difficult to obtained homogenous, well-dispersed suspension of high solid content. Surface chemical properties are influenced by many factors, such as the nature of the ceramic particles, size distribution, surface impurities, nature of solvent, pH value.[3,5–7] In such a high solid loading system, the particles have a tendency toward agglomeration. This may increass the viscosity of mixtures and decrease their moldability. The agglomerates can in principle be studied by using the electron microscopy techniques (for example scanning electron microscopy SEM). However, it is difficult to identify individual agglomerates in the mixture because of high packing density of the powder. Moreover, the examination

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doi:10.1016/j.jeurceramsoc.2006.07.013

is carried out in a gaseous medium or in vacuum, so the sample needs to be dried that severely disturbs the real structure of aggregates in suspensions.

Experimental evidence suggested that the degree of agglomeration of particles in suspensions can be most directly assessed by the dynamic viscosity measurement studied usually for the high volume concentration range of suspensions.[8,9] This limits the accuracy of such measurements because of the lack of an appropriate theoretical model of viscosity for high concentration range.

Therefore, the goal of this paper is to prove experimentally that the structure of ceramic suspensions, in particular the agglomeration degree can be accurately determined from low volume fraction viscosity measurements. We have chosen for our studies zirconia, which is extensively used in ceramic industry, for producing biocompatible coatings and in the investment casting industry for producing forms of exceptional temperature resistance. As the model organic dispersant we have selected the anionic polyelectrolyte:poly(sodium 4-styrenesulfonate) (PSS), which is stable over a wide range of pH and ionic strength.[10] Additionally, its molecular structure, charge and conformation in solutions are well characterized.[11]

2. Experimental

2.1. Materials and methods

The zirconia oxide used in this work was a commercial powder (nominal size fraction < 1 μm, purity > 99.5%) from Alfa Aeaser a Johnson Matthey company. Anionic poly(sodium 4-styrenesulfonate (PSS), Mw = 70 000 g/mol) was purchased from Aldrich. Solutions of PSS were prepared by dissolving polyelectrolytes in deionized water and subsequent filtration using the 0.22 μm filter. The pH was adjusted with standard analytical grade HCl or NaOH solutions.

The specific surface area of the zirconia powder, determined by means of N_2 adsorption using B.E.T. multipoint method (Quantasorb Jr., Quantachrome, USA), was 5.0 m^2/g. The phase and crystal structure of zirconia oxide was identified by X-ray diffraction (XRD Philips). The analysis shows that the the zirconia powder has a monoclinic structure. The estimation of zirconia particle (or aggregate) diameter in aqueous solution was performed by dynamic light scattering (Malvern Zetasizer Nano AS).

The zeta potential of zirconia suspension was measured by the microelectrophoretic method using Malvern Zetasizer Nano ZS apparatus. The ionic strength was adjusted using NaCl solution. Each zeta potential was averaged from 10 measurements. All measurement were performed at 293 K. For sake of convenience all the physicochemical data characterizing the zirconia are collected in Table 1.

Table 1
Physicochemical data of zirconia

Property	Value	Remarks
Average particle size, standard deviation (μm)	0.64, 0.4	Malvern PCS, pH 10, $I = 10^{-3}$ M
Specific surface area (m^2/g)	5	BET
Zeta potential (mV)	−58	Electrophoresis, pH 10, $I = 10^{-3}$ M
pH suspension	10	
pH of the isoelectric point	4.7	Malvern Zetasizer, titration method
Specific density (g/cm^3)	5.47, 5.79	Suspension dilution, producer
Apparent density (g/cm^3)	3.04	Viscosity measurements

The dynamic viscosity of colloidal zirconia and PSS as a function of the volume concentration was measured using a home made capillary viscometer in vertical orientation. Automatic detection of suspension level via electric conductivity proved very useful for non-transparent suspensions. In each experiments, the flow rate time t of the suspension volume $v_{\text{sus}} = 10\,\text{cm}^3$, through capillary with internal diameter, R, was measure. The average flow rate was determined from the dependence $\langle V \rangle = v_{\text{sus}}/\pi R^2 t$, where t is the time of passing the suspension through the capillary.

The temperature of measurements was maintained at 293 K, using a thermostat. Various capillaries of internal diameter ranging from 0.5 to 2 mm were used, depending on the viscosity range. The device was calibrated using pure liquids of known viscosity, such as, water, butyl and amyl alcohols or ethylene glycol. The accuracy of viscosity determination for the range 1–10 mPa s was estimated to be 0.5% with the main source of error stemming from the suspension density measurements.

The zirconia suspensions of the volume fractions in the range of 0.005–0.07, were prepared by dispersing zirconia powder in distilled water or in of the appropriate PSS solutions concentration, at a pH adjusted by the standard solution of 0.1 M NaOH. The amount of PSS required to form monolayer on the zirconia particles surface was first dissolved in distilled water, then the zirconia powder was added to the solution. The suspension was ultrasonicated for 30 min in order to break up aggregates and to remove traces of gases. Every data point of the dynamic viscosity was an average of five measurements.

The amount of polyelectrolyte adsorbed onto zirconia was determined using the solution depletion method. After mixing the zirconia suspension with the polyelectrolyte solution, at the required concentration (depending on the volume fraction of zirconia powder) under vigorous stirring, the mixture was centrifuged at 10,000 rpm for 30 min. The time assured a complete sedimentation of the particles. The supernatant was decanted and the concentration of unadsorbed PSS was determined by UV spectroscopy at a wavelength of 225 nm.

Zeta potential of PSS was determined by using the Malvern Zetasizer Nano ZS. The effect of pH was studied for the range of 3–10.

2.2. Physicochemical characteristics of zirconia

The size distribution of zirconia suspensions prepared according to the above procedure at pH 10 and $I = 5 \times 10^{-3}$ M, is shown in Fig. 1a. As can be observed, the size distribution of the suspension is rather broad and asymmetrical with the main peak at 0.5 μm. This suggests that a significant fraction of aggregates was present in the zirconia suspension. The averaged particle

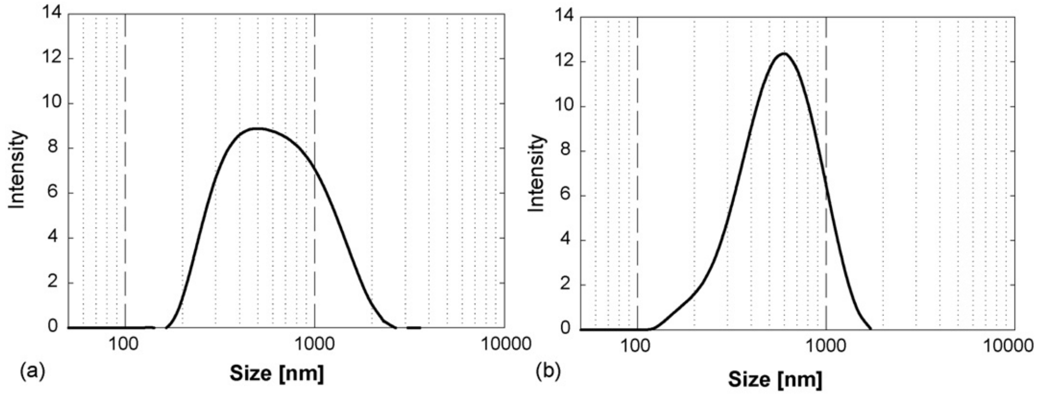

Fig. 1. Particle size distribution of zirconia determined by the PCS method. (a) ZrO_2 at pH 10, $I = 5 \times 10^{-3}$ M, averaged particle size 0.64 μm, standard deviation of the size 0.40 μm. (b) ZrO_2 with PSS at pH 10, $I = 5 \times 10^{-3}$ M, averaged particle size 0.56 μm, standard deviation of the size 0.25 μm.

diameter was 0.64 μm with the standard deviation of 0.40 μm. A similar but more narrow size distribution was obtained for zirconia suspension in PSS solution at pH 10 and $I = 5 \times 10^{-3}$ M as can be seen in Fig. 1b. The averaged particle diameter was 0.56 μm with the standard deviation of 0.25 μm.

The size of primary particle of zirconia was determined by the scanning electron microscopy (SEM). From the SEM images (shown in Fig. 2) it was estimated that the size of primary particles was 0.2 μm. It is interesting to compare this value with the BET data, giving specific surface area $S = 5.0$ m^2/g as mentioned previously. By assuming a spherical shape of the particles and using the formula $d = 6/\rho_p S$ (where ρ_p is the specific density of the solid zirconia, equal 5.79 g/cm^3, as specified by the producer) one obtains $d = 0.21$ μm. As can be noticed this is similar to the primary particle size derived from the SEM observations.

3. Result and discussion

It is known that the stability and aggregation degree of oxides, in particular zirconia, depends to a critical extent on pH value that governs the number of hydroxyl groups increasing the negative charge of particles. The increase in the surface charge usually increases the absolute value of the zeta potential of particles (the electric potential in the slip plane) which results in an increased stability of suspensions.[12] The zeta potential is a quantity well accessible experimentally, e.g., by using the microelectropheretic method as done in this work. The dependence of the zeta potential of ZrO_2 suspensionon on the pH determined for a fixed ionic strength of 10^{-3} M is shown in Fig. 3. As can be noticed, for pH 4.7, the zeta potential of the suspension of pure zirconia was close to zero. This pH value is referred to as the isoelectric point. In this respect our data agree well with that reported by Ewais et al.[3] and Crucean et al.[13,14] On the other hand, Fengqiu et al.[5] reported pH 6 as the isoelectric point. Generally, there is a rather large spread in the reported data, e.g., Johnson et al.[6] reported pH 7.5 as the isoelectric point of zirconia. This issue is discussed at length in the book of Kosmulski.[14]

These high values of zeta potential (in absolute terms) are expected to stabilize of the zirconia suspension. However, the dispersion of aggregates seems rather unlikely. This hypothesis was tested by using the dynamic viscosity measurements. However, a prerequisite of a correct interpretation of viscosity measurements is the knowledge of the volume fraction of the solid in the suspensions Φ_V. This quality can only be calculated if the real density of particles in suspension is known. The density was determined by the dilution method, i.e., from the dependence of the suspension density on the weight fraction of zirconia $w = m_p/m_{sus}$, where m_p is the particle mass

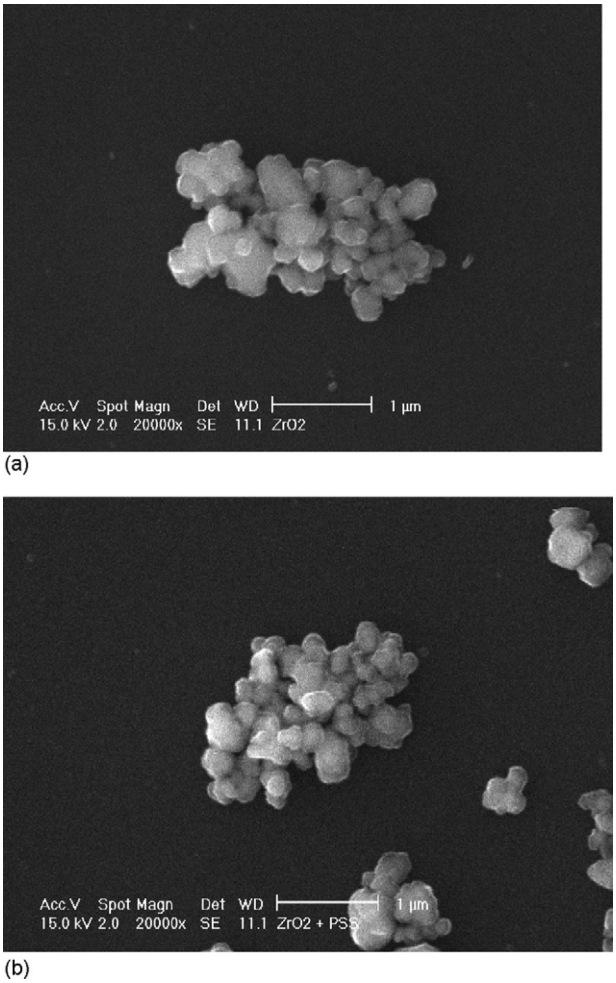

Fig. 2. SEM image of zirconia powder deposited on mica surface: (a) ZrO_2 and (b) ZrO_2 with PSS.

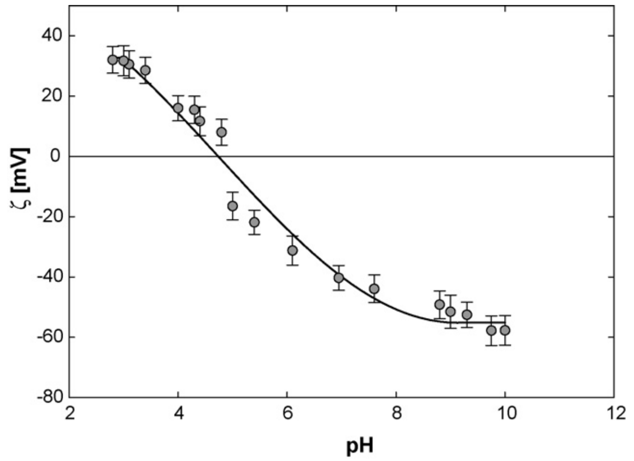

Fig. 3. Zeta potential of ZrO_2 as a function of pH determined for $I = 1 \times 10^{-3}$ M.

and m_{sus} is the suspension mass. The weight fraction of zirconia was changed within the range 0–0.3 by taking appropriate mass of the zirconia powder and the solvent (electrolyte). By assuming that the volume of the electrolyte remained the same upon mixing, the density of the zirconia/electrolyte mixture can be expressed by the formula[8]:

$$\rho_{sus} = \rho_e \frac{1}{1 + w(\rho_e/\rho_p - 1)} \qquad (1)$$

where ρ_e is the solvent (electrolyte density) and ρ_p is the density of zirconia oxide particles (dry).

From Eq. (1) one can deduce that zirconia particle density in the suspension can be calculated from the dependence:

$$\rho_p = \frac{\rho_e}{1 + \operatorname{tg}\alpha} \qquad (2)$$

where $\operatorname{tg}\alpha$ is the slope of the ρ_e/ρ_{sus} versus w dependence (which is negative in our case) that is expected to be a straight line. The results shown in Fig. 4 suggest that these dependencies can well be fitted by a linear regression line with the slope which gives for the zirconia oxide density 5.47 g/cm^3. This is slightly smaller than the value supplied by the producer for solid zirconia, equal 5.79 g/cm^3. The deviation is probably caused by the intrinsic porosity of zirconia particles. Some of the pores of primary particles forming aggregates were probably closed, inaccessible for the solvent. By knowing the real density of particles, the volume fraction can be calculated as $\Phi_V = w\rho_{sus}/\rho_p$.

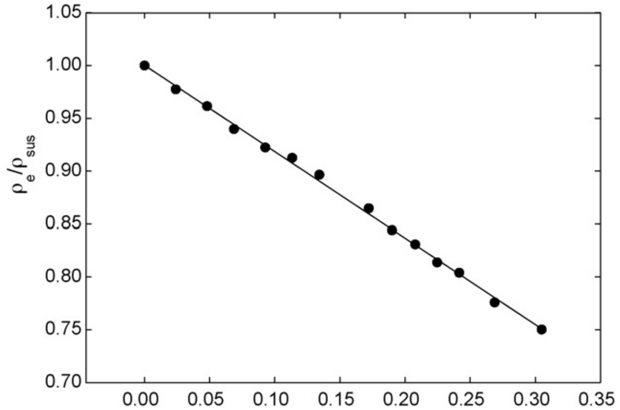

Fig. 4. The dependence of ρ_e/ρ_{sus} on the weight fraction w of ZrO_2, determined for pH 10.

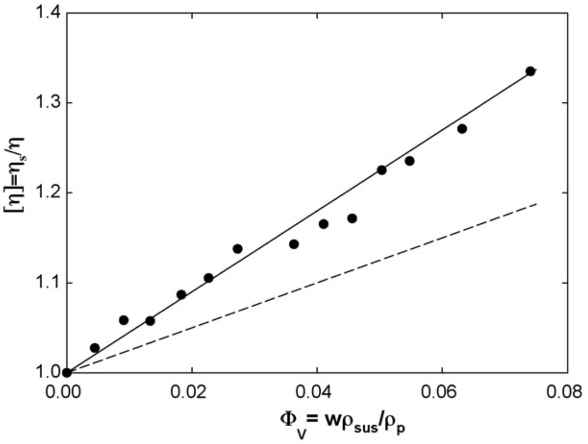

Fig. 5. The dependence of the intrinsic viscosity $[\eta] = \eta_s/\eta$ of ZrO_2 suspensions on the volume fraction $\Phi_V = w\rho_{sus}/\rho_p$ determined for pH 10, $I = 5 \times 10^{-3}$ M. The broken line denotes the theoretical results calculated from Einstein formula $\eta_s/\eta = 1 + 2.5\Phi_V$ and the solid line represent the linear regression fit.

Typical experimental data presenting the dependence of the intrinsic viscosity $[\eta] = \eta_s/\eta$ (where η_s is the viscosity of the suspension and η is the viscosity of the electrolyte) on the volume fraction of zirconia for the low concentration range ($\Phi_V < 0.08$) are plotted in Fig. 5. It is interesting to note, that the weight fraction of zirconia in these suspensions was much higher attaining 0.4 (for $\Phi_V = 0.08$). As can be seen, the dependence of $[\eta]$ on Φ_V of zirconia can well be fitted by a linear regression. However, the slope of this line $d[\eta]/d\Phi_V$ was found larger than the Einstein formula predicts, written in the usual form:

$$\bar{\eta} = \frac{\eta_s}{\eta} = 1 + C_V \Phi_V \qquad (3)$$

were C_V is the dimensionless constant.

In our case the slope was found equal 4.5, in stead of 2.5, which is 1.8 times larger than predicted by the Einstein formula.

The deviation from the Einstein formula occurring for the low volume fraction of suspensions is interpreted in terms of the primary electroviscous effect stemming from shear induced deformations of ionic double layers surrounding suspended particles.[15] This leads to increased dissipation of mechanical energy resulting in increased viscosity of suspensions over values predicted by the Einstein model. This deviation is expressed in terms of the primary electroviscous function, expressed as[16–19]:

$$C_V = 2.5(1 + p) \qquad (4)$$

where p is the primary electroviscous function depending on the ionic strength and composition of the electrolyte.

In the case where the diffusion coefficients of ions forming the electrolyte do not differ too much, one can derive an analytical expression for p, valid for spherical particles[18]:

$$p = \frac{2\varepsilon\zeta^2(1+\kappa a)^2 F(\kappa a)}{3\pi\eta D_i} \quad (5)$$

where ε is the dielectric constant of water (relative permittivity), ζ the zeta potential of the particle forming the suspension, D_i the ith ion diffusion coefficient, $F(\kappa a)$ the function of the dimensionless κa parameter, $\kappa^{-1} = (\varepsilon\ kT/8\pi e^2 I)^{1/2}$ the double-layer thickness, k the Boltzmann constant, T the absolute temperature, e the elementary charge, I the ionic strength of solution and $a = d/2$ is the particle radius.

For a ionic strength of $I = 3 \times 10^{-3}$ M, κa equals 56 for the zirconia suspensioun (assuming 0.6 μm as the averaged diameter of the aggregate). As calculated in[18] for this value of κa, the value of the function $(1 + \kappa a)^2 F(\kappa a)$ is about 3×10^{-4}. Then, by taking $\zeta = -50$ mV and $D = 2 \times 10^{-5}$ cm^2/s one can estimate from Eq. (5) that $p = 7 \times 10^{-4}$. As can be seen, this value is more than three orders of magnitude smaller than experimentally found for zirconia, equal 0.8. The comparison proves quite unequivocally, that the primary electroviscous effect is not responsible for the deviation of zirconia suspension viscosity from the Einstein model.

Therefore, the most probable reason of this deviation can be sought in the presence of aggregates in the suspension. For aggregates of non-spherical shape, the increase in the intrinsic viscosity of suspensions occurs because of the increase in the fluid velocity gradients due to particle rotation. This effect was described quantitatively by Brenner[19] for spheroidal particles, having both a prolate and an oblate shape. The parameter of primary significance governing suspension viscosity in this case is the Peclet number (for rotary Brownian motion) defined as the ratio of the characteristic rotation velocity $\langle G\rangle d$ to the diffusion velocity D/d:

$$Pe = \langle G\rangle \frac{d^2}{4D} \quad (6)$$

where $\langle G\rangle$ is the averaged shear rate in the capillary, $D = kT/3\pi\eta d$ the diffusion coefficient of the aggregate and d is the typical diameter of the aggregate.

In the case of the capillary viscometer the averaged shear rate can be calculated as

$$\langle G\rangle = \frac{8v_{\text{sus}}}{3\pi R^3 t} \quad (7)$$

By taking the typical experimental data: $R = 0.035$ cm, $v_{\text{sus}} = 10$ cm^3, $t = 50$ s, one obtains $\langle G\rangle = 4 \times 10^3$ s^{-1}. Using this value and taking $d = 0.66$ μm as the averaged size of the zirconia aggregate one can calculate from Eq. (7) that $Pe = 6.6 \times 10^2$. Such a large value of Pe indicates that the suspension viscosity was dominated by shear rather than diffusion. Thus, in the limit of such large Peclet numbers, the intrinsic viscosity of particle suspensions attains the limiting, high-shear values, tabulated by Brenner.[19] For prolate spheroids having the length to width aspect ratio of 3 the limiting value of $[\eta] = 2.684$, for aspect ratio 4, $[\eta] = 2.801$ and for aspect ratio 5, $[\eta] = 2.918$. As can be noticed, even for very elongated spheroids, i.e., for aspect ratio 5, the correction to the Einstein's formula is about 12%. It seems, therefore, that the non-spherical shape of zirconia particle aggregates is not responsible for the deviation of the slope of $[\eta]$ versus Φ_{V} dependence from the from Einstein's formula, which was, as previously estimated, about 180%.

The most likely explanation is that the zirconia aggregates form a loose structure, characterized by a high degree of porosity, as suggested by the SEM picture shown in Fig. 2. As a result, the effective hydrodynamic volume of particles in the suspension (at fixed mass fraction) becomes larger than the net volume of isolated primary particles, which results in a decreased apparent density of particles. A similar model was effectively used before to explain the anomalous viscosity behavior of silica suspensions.[8] It was postulated that upon contact with water, a gel-like layer was formed on the surface of silica, having lower apparent density than the core volume of particles.

Since the primary electroviscous effect remains negligible as previously estimated, the apparent density of the aggregates can be calculated from the dependence[8]:

$$\rho^* = \frac{2.5\rho_{\text{p}}}{C_{\text{V}}} \quad (8)$$

By knowing the apparent density, one can calculated the average porosity of aggregates ε_p from the formula[8]:

$$\varepsilon_{\text{p}} = \frac{\rho_{\text{p}} - \rho^*}{\rho_{\text{p}} - \rho_{\text{e}}} \quad (9)$$

By substituting into Eq. (9) the data obtained in our experiments, i.e., $\rho_{\text{p}} = 5.47$ g/cm^3, $\rho^* = 3.03$ g/cm^3, $\rho_{\text{e}} = 1.01$ g/cm^3 one obtains $\varepsilon_{\text{p}} = 0.55$. Hence, the apparent volume fraction of solid in the aggregate equals $1 - \varepsilon_{\text{p}} = 0.45$. This seems a quite reasonable estimate in view of the fact that the maximum packing of spheres in three dimensions is 0.62.[20] Our value is smaller because the aggregate structure is more loose than under the maximum packing when, be definition, all particles must contact with each other.

Having established the basic relationship for the pure zirconia suspension, we have studied the effect of the anionic polyelectrolyte PSS on the viscosity of zirconia suspension. This polyelectrolyte, bearing sulfonic groups in chain was thoroughly characterized in our previous work.[11] The extended length of the polyelectrolyte chain, having the molecular weight of 70,000 is 91 nm and the length to diameter ratio of the chain equals 78. One can draw quantitative conclusions about the ionization degree of the PSS chain from the electrophoretic mobility measurements as a function of the pH and ionic strength. The data compiled in Table 2 show that the zeta potential of PSS increased from -90 ± 5.0 mV for $I = 1 \times 10^{-3}$ M to -55 ± 5.0 mV for $I = 0.15$, that suggests a significant reduction in the number of

Table 2
Zeta potential ζ_{p} of PSS (mV) at pH 10

I (M)	Zeta potential (MV)
1×10^{-3}	-90 ± 5.0
5×10^{-3}	-83 ± 5.0
1×10^{-2}	-74 ± 5.0
0.15	-55 ± 5.0

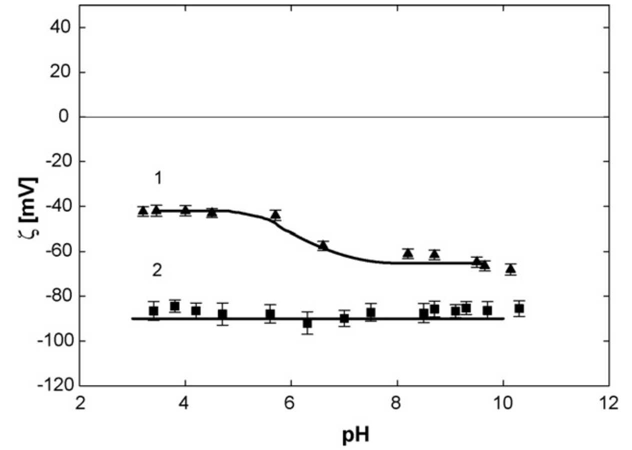

Fig. 6. Zeta potential as a function of pH determined for $I = 1 \times 10^{-3}$ M. (▲) ZrO_2 with PSS (curve 1); (■) PSS (curve 2).

ionic groups at the PSS molecule surface. On the other hand, the dependence of the zeta potential of PSS on pH of the solution measured for a fixed ionic strength $I = 1 \times 10^{-3}$ M is shown in Fig. 6. As can be seen, for the pH range studied, i.e., 5–10 the zeta potential of PSS remains fairly constant that suggests a pH- independent ionization degree of surface groups of this molecule.

The result of viscosity measurements of PSS solutions performed for PSS volume fraction range $\Phi_V < 0.004$ and the ionic strength of $I = 5 \times 10^{-3}$ M and 0.15 M are presented in Fig. 7. As can be seen, the dependence of $[\eta]$ on Φ_V for both ionic strength can well be fitted by a linear regression. The slope of these lines $d[\eta]/d\Phi_V$ was found equal to 50 for $I = 5 \times 10^{-3}$ M and 25 for $I = 0.15$ M. This is again much higher than the Einstein formula predicts for spherically shaped particles. It seems that a proper interpretation of these data can be sought in the highly non-spherical shape of PSS molecules in solutions. Again, these data can be interpreted in terms of the Brenner model.[19] However, in the case of PSS, the rotary Peclet number assumes much smaller values than for zirconia because of much higher diffusion coefficient of PSS. By taking $\langle G \rangle = 4 \times 10^3\ \mathrm{s}^{-1}$, $L = 91$ nm (extended molecule length) and $D = 1.8 \times 10^{-7}\ \mathrm{cm}^2/\mathrm{s}$ (for $I = 5 \times 10^{-3}$ M) one can calculate from Eq. (7) that $Pe = 0.46$. For higher ionic strength this should be definitely smaller because of the smaller length of the molecule. Since this value is smaller than unity, the suspension viscosity is dominated by the rotary diffusion of PSS molecules rather than by the shear as was the case for the zirconia suspension. In this limit, of diffusion dominated viscosity Brenner[19] derived the approximate formula describing the intrinsic viscosity of prolate spheroid polymer solution:

$$[\eta] = \frac{\bar{L}^2}{15}\left[\frac{3}{\ln 2\bar{L} - 0.5} + \frac{1}{\ln 2\bar{L} - 1.5}\right] + \frac{8}{5} \qquad (10)$$

where $\bar{L} = L/d$ is the ratio of the length to width of the spheroid.

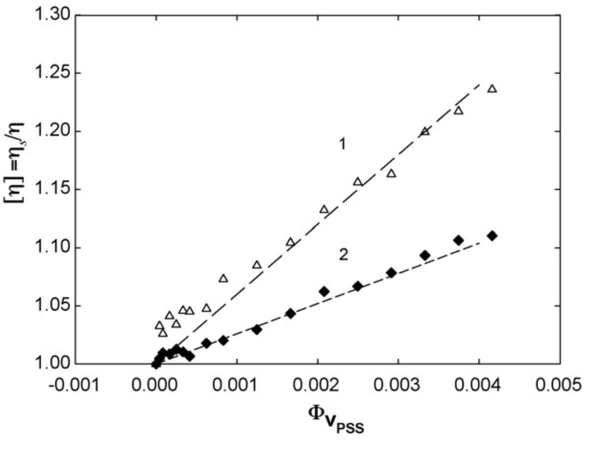

Fig. 7. The dependence of the intrinsic viscosity of PSS $[\eta] = \eta_s/\eta$ on its volume fraction Φ_V, pH 6.5–10, (△) $I = 5 \times 10^{-3}$ M (curve 1) and (♦) $I = 0.15$ M (curve 2).

It can be calculated from Eq. (10) that for $\bar{L} = 78$ (the value pertinent to the extended PSS molecule) $[\eta] = 383$, for $\bar{L} = 50$ (the molecule bend to the form of a semi-circle) $[\eta] = 177$ and for $\bar{L} = 25$ (the molecule bend to the form of a circle) $[\eta] = 55$. As can be seen, the latter intrinsic viscosity agrees well with the experimental value obtained for the ionic strength of 5×10^{-3}.

After measuring the viscosity of zirconia and PSS separately, the viscosity of mixtures was studied in order to estimate the improvement in the fluidity upon the addition of PSS. The fluidity can be increased by increasing the dispersion degree of the powder promoted by adsorption of PSS. The amount of polyelectrolyte adsorbed on zirconia was determined by the solution depletion method. It was found that irrespective on the initial concentration of PSS in the suspension (varied between 1000 and 5000 ppm) the amount of PSS adsorbed on particles was almost constant and equal 2.5×10^{-3} g per one gram of the zirconia powder (this corresponds to 5×10^{-4} g per square meter of the dry powder). By taking the affective cross-section of the PSS molecule as 91 × 11 nm ($1.06 \times 10^{-16}\ \mathrm{m}^2$) one can estimate that the amount of adsorbed PSS corresponds to the dimensionless surface coverage of 0.45, which seems a quite reasonable value in view of previous estimates.[21]

Adsorption of PSS on zirconia decreased significantly the zeta potential of particles for the entire range of pH (see Fig. 6). This is fully in accordance with the results of Fengqiu et all.[5] who determined zeta potential of zirconia powder in solutions of Darvan C (an anionic polyelectrolyte with carboxylic groups). It was observed that for pH > 3 zeta potential of zirconia became negative upon adsorption of Darvin C attaining a minimum value of −60 mV for pH 8. It is not obvious what is the physical mechanism of adsorption of anionic polyelectrolytes (PSS and Darvin C) on negatively charged zirconia surface, which is the case for pH > 5 as can be deduced from the data shown in Fig. 3. It seems that a possible explanation of this fact is the heterogeneous nature of zirconia particles dispersed in solution. Hence, adsorption of PSS may occur on surface areas bearing locally a positive charge in the nanoscale, although the net charge of zirconia surface, in the microscale, remains negative. Certainly, a unequivocal confirmation of this hypothesis requires further systematic studies, which are outside the scope of this work, however.

It is interesting to mention that, in contrast to the results reported by Fengqiu et al.[5] in our case, adsorption of PSS on zir-

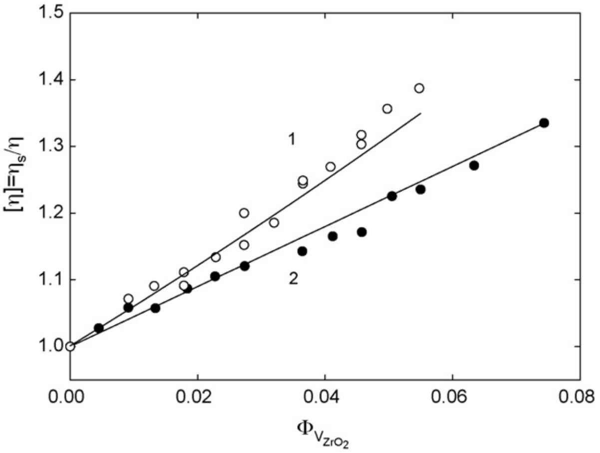

Fig. 8. The dependence of the intrinsic viscosity $[\eta]=\eta_s/\eta$ ZrO_2 vs. the volume fraction $\Phi_V = w\rho_{sus}/\rho_p$, pH 10, $I=5\times10^{-3}$ M. (●) ZrO_2, the line denotes the linear regression $[\eta]=1+4.5\,\Phi_{V_{ZrO_2}}$ (curve 2); (○) ZrO_2 + PSS mixture, the solid line denoted the product of intrinsic viscosities $[\eta]=[\eta]_{ZrO_2}+[\eta]_{PSS}=(1+4.5\,\Phi_{V_{ZrO_2}})+(1+50\,\Phi_{V_{PSS}})$ (curve 1).

conia did not increase too significantly the dispersion degree of aggregates. This is evident from the particle size measurements showing that the average size of zirconia particles dispersed in PSS (at pH 7.4) was 0.56 μm, which does not differ much from the value observed in PSS free solutions. The limited influence of PSS on the dispersion degree of zirconia also was confirmed by the viscosity measurements whose results are shown in Fig. 8. As can be seen, the dependence of the intrinsic viscosity of zirconia dispersed in PSS solution (variable polymer concentration from 350 ppm to 2000 ppm, pH 10, $I=5\times10^{-3}$ M) on the volume fraction solid can well be fitted by a line with the slope being the product of the viscosity of zirconia dispersed in PSS free solution of the same composition and the viscosity of PSS alone. Hence, our results seem to confirm the effective medium hypothesis[22] according to which the relative viscosity of a suspension having the solid concentration $\Phi_{V_1}+\Phi_{V_2}$ (where Φ_{V_1} is the volume fraction of zirconia and Φ_{V_2} is the volume fraction of PSS) equals to the product of relative viscosities $\bar{\eta}(\Phi_{V_1})\bar{\eta}(\Phi_{V_2})$.

4. Concluding remarks

It has been demonstrated experimentally that the relative viscosity of dilute zirconia suspensions increased more rapidly with the volume fraction that the Einstein formula predicted. This discrepancy could not be explained in terms of the primary electroviscous effect because of small thickness of the electric double-layer. As a plausible explanation the presence of aggregates in the zirconia suspension was given, which were composed of primary particles of the size ca. 200 nm. The hypothesis of the presence of aggregates was also confirmed by the SEM. The viscosity measurements allowed one to determine the averaged solid content in these aggregates, which was found close to 0.45.

Analogous measurements of the viscosity of the anionic polyelectrolyte-PSS used to enhance the stability of zirconia suspensions showed that the slope of the intrinsic viscosity vs. volume fraction attained values as high as 50 for $I=5\times10^{-3}$ M. This effect was interpreted in terms of the flexible rod model. According to this model, for higher electrolyte concentration, the PSS molecule assumes the shape of a semi circle or sinusoidal curve rather than a random coil structure as often suggested.

It was further confirmed experimentally that adsorption of PSS on zirconia decreased significantly the negative zeta potential but did not influence too significantly the dispersion degree of zirconia particles. Also the viscosity of the zirconia suspension in PSS solutions was found equal to the product of the viscosity of zirconia dispersed in PSS free solution of the same composition and the viscosity of PSS alone.

Acknowledgements

This work was supported by MNiSW Grant 4T08B 03425.

The help of Ms. K. Kusak in performing the experiments is kindly acknowledged.

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