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INFLUENCE OF PARTICLE SHAPE ON THE VISCOSITY OF KAOLIN SUSPENSIONS

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ABSTRACT
The influence of particle shape (aspect ratio) on the intrinsic viscosity is investigated, taking three Czech kaolin products (floated kaolins) as paradigmatic examples. An average aspect ratio is obtained for each kaolin from a comparison of particle size measurements using sedimentation and laser diffraction. The intrinsic viscosity is obtained by a multistep procedure: firstly, flow curves are recorded for each kaolin with the optimum deflocculant concentration, secondly, the (apparent) relative viscosities read off from the flow curves are plotted against the kaolin volume fraction and, thirdly, these data are fitted using the Krieger relation to obtain the intrinsic viscosity in the asymptotic dilute limit. It is shown that the data determined with the method proposed are within the Jeffery and Brenner bounds and that an average aspect ratio of about 20 (17-22) results in an intrinsic viscosity of about 10 (7-13), compared to 2.5 for spherical particles. Although currently the measurement precision is not sufficient to seriously assess the influence of Brownian motion, the method can principally be used to predict the intrinsic viscosity when the average aspect ratio of the system (and its particle size distribution) is known, and vice versa.

KEYWORDS: kaolin, particle shape, viscosity

INTRODUCTION

It is well known that particle shape has a decisive influence on suspension rheology. In particular, for kaolin suspensions, where the degree of anisometry is generally high (due to the platey shape of the kaolinite crystals), it may be expected that the effective viscosity exhibits a steeper increase with concentration than suspensions with isometric or spherical particles. A quantitative measure of the shape anisometry of particles is the aspect ratio R, which can be defined as the ratio of the longest to the shortest dimension, i.e. in the case of oblate particles (oblate spheroids, cylinderical disks or platelets) the ratio of the equatorial diameter to the height or thickness:

$$R = \frac{diameter}{thickness}. \tag{1}$$

A convenient measure of the viscosity increase is the so-called "intrinsic viscosity" (or Einstein-Jeffery coefficient), which is defined as the initial slope of the relative-viscosity-versus-solids-volume-fraction curve in the dilute limit, i.e. the expression

$$[\eta] = \lim_{\phi \to 0} \frac{\eta_r - 1}{\phi}, \tag{2}$$

where ϕ is the solids volume fraction and $\eta_r = \eta/\eta_0$ the relative (or reduced) viscosity, defined as the ratio of the effective viscosity of the suspension η to the viscosity of the dispersing medium η_0. In this work we apply a simple approximate method proposed by Pabst and Berthold (2007) to determine the average aspect ratio of three types of kaolin products (floated kaolins). The intrinsic viscosity of the corresponding kaolin suspensions is extracted from extensive viscometric measurements and compared with theoretical models available in the literature.

THEORETICAL – RHEOLOGY OF OBLATE PARTICLE SUSPENSIONS

The first work on the rheology of anisometric particle suspensions (Jeffery, 1922) concerns ellipsoids. In Jeffery's paper an explicit analytical solution is presented, and minimum and maximum values of the intrinsic viscosity in dependence of the aspect ratio are given for (prolate and) oblate spheroids. Later work by Brenner (1974) showed that Jeffery's bounds were too wide and that the complete solution can be given in the form

$$[\eta] = 5Q_1 - \frac{15}{4} Q_2 \left\langle \sin^2\theta \right\rangle - \frac{5}{4B}\left(3Q_2 + 4Q_4\right) \cdot \left\langle \sin^2\theta \cos 2\varphi \right\rangle + \frac{15}{2BP}\left(3Q_2 + 4Q_3\right)\left\langle \sin^2\theta \sin 2\varphi \right\rangle, \tag{3}$$

(Equation 3) where $B = 5N/3K_r$ is a dimensionless parameter and $P = \gamma/D_r$ the rotary Péclet number, with $\dot{\gamma}$ being the shear rate and the rotary diffusion coefficient D_r given by the Stokes-Einstein equation

$$D_r = \frac{kT}{6\,V\eta_0 K_r}\,, \tag{4}$$

where k is the Boltzmann constant, T the absolute temperature, V the particle volume and η_0 the viscosity of the suspending medium. The angular brackets denote averaging over all orientations (with polar angle θ and azimutal angle φ) and the material constants N and K_r as well as Q_1, Q_2, Q_3, Q_4 are rather complicated functions of the aspect ratio, given in (Brenner, 1974). They are too lengthy to be written out here in explicit form. Note that Brenner's equation accounts for (rotary) Brownian motion via the rotary Péclet number (rotary diffusion coefficient). In the case of dominant Brownian motion (i.e. a very high rotary diffusion coefficient or a very low shear rate) Brenner's equation reduces to the upper bound ("zero shear rate limit")

$$[\eta]_0 = 5Q_1 - Q_2 + 2Q_3\,. \tag{5}$$

This equation (analytical solution) is in extremely good agreement with the numerical solution values obtained by Scheraga (1955) and is at the same time rather close (except for an additive constant) to the remarkably simple approximate solutions of Simha (1940) and Kuhn and Kuhn (1945), which are

$$[\eta]_0 = \frac{16}{15\,R\arctan\left(R^{-1}\right)}\,, \tag{6}$$

$$[\eta]_0 = \frac{4}{9} + \frac{32}{15\,\pi\,R}\,, \tag{7}$$

respectively. Inserting into Equation 5 the explicit expressions given for Q_1, Q_2, Q_3 in Brenner's paper (Brenner, 1974), it can easily be verified that for oblate particles with aspect ratios up to 50 the linear relation $[\eta]_0 \approx 1.45 + 0.672 \cdot R$, which is the best linear fit in this range, is a reasonably precise approximation to Equation 5.

EXPERIMENTAL – MATERIALS AND METHODS

Three Czech kaolin products (floated kaolins) have been investigated in this work: KDK (Kaolin Hlubany a.s., Podbořany), Imperial (Sedlecký kaolin a.s., Božičany), SpEX (Keramika Horní Bříza a.s., Kaznějov). All three are commercially available, well specified kaolin grades and are denoted by their trademark labels in this work. The particle size distributions have been measured via sedimentation in Andreasen cylinders and via laser diffraction (using the Fraunhofer approximation) on a Fritsch Particle Sizer Analysette 22 Nanotec (Fritsch Laborgerätebau GmbH, Germany). An average aspect ratio has been calculated from the difference between the two size distributions, using the relation

$$R = \pi \cdot \left(\frac{D_{50}^L}{D_{50}^S}\right)^2\,, \tag{8}$$

where D_{50}^L and D_{50}^S are the median sizes (median equivalent sphere diameters) measured via laser diffraction and sedimentation, respectively. This relation has been derived recently (Pabst and Berthold, 2007), using a modified Stokes law for oblate spheroids and taking into account random orientation in the laser diffraction measurement via Cauchy's stereological theorem. Note that Equation 8 is an approximation for sufficiently high aspect ratios. Moreover, due to the possible (slight) dependence of the D_{50}^L values on the laser diffraction equipment, in particular the algorithm applied to deconvolute the diffraction pattern, absolute values must be considered with due caution. However, in spite of its deficiencies, it seems that Equation 8 represents to date the only viable route to extract an average aspect ratio of a particle system (with oblate particles). A similar relation is available for use with microscopic image analysis, see (Pabst and Berthold, 2007). The disadvantage of the latter route is that information on the average thickness of the platelets must be determined independently.

Sodium pyrophosphate (Penta a.s., Czech Republic) was used as a deflocculant for the sedimentation, laser diffraction, and rheological measurements. The optimum deflocculant content was determined individually for each kaolin by recording the flow curves of 10 wt. % kaolin suspensions with different deflocculant content, see Figure 1. It has to be emphasized that the degrees of deflocculation (and delamination) have a decisive effect on the rheological behavior of kaolin suspensions, see e.g. (Loginov et al., 2008; Moan et al., 2003; Sjöberg et al., 1999). Therefore care has been taken to perform all measurements in this paper with identically prepared suspensions.

It is evident that kaolin suspensions without deflocculant typically exhibit shear-thinning behavior whereas well deflocculated systems show a rheological behavior close to Newtonian. All suspensions were prepared by 1 h homogenization in a polyethylene bottle with alumina balls and 1 min ultrasonication (ultrasonic processor UP200S with titanium sonotrode S14, Dr. Hielscher GmbH, Germany).

Flow curves of well deflocculated kaolin suspensions with different solids contents were measured by rotational viscometry (RotoVisco 1 with concentric cylindrical sensor Z41, ThermoHaake

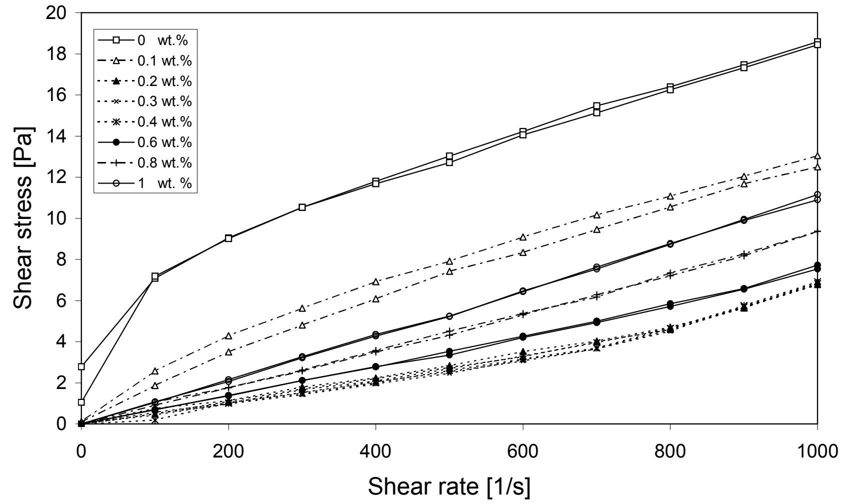

Fig. 1 Flow curves of suspensions with 10 wt.% kaolin KDK and different deflocculant contents (in the range between 0 and 1 wt.%, related to solids).

GmbH, Germany) in the shear rate range between 0 and 1000 s^{-1}. Apparent viscosities were extracted for shear rates of 200, 400, 500, 600, 800 and 1000 s^{-1} and subsequently used for plotting graphs of the relative viscosity η_r (using a value of 1 mPas for water at room temperature) versus the kaolin volume fraction ϕ. The $\eta_r - \phi$ data points were finally fitted using the Krieger relation (Krieger, 1972),

$$\eta_r = \left(1 - \frac{\phi}{\phi_C}\right)^{-[\eta]\phi_C}, \tag{9}$$

in order to extract the intrinsic viscosity $[\eta]$ (the critical volume fraction ϕ_C is an asymptotic value, corresponding to the maximum solids loading that the suspension may contain without loosing the ability to flow). A completely analogous procedure has been applied to isometric particles by Gregorová et al. (2006, 2008) and to prolate particles (short fiber systems) in Pabst et al. (2006). For the theoretical status of the Krieger relation, Equation 9, and its relation to other analogous power laws, the reader may consult (Pabst, 2004) and (Pabst et al., 2007).

RESULTS AND DISCUSSION

Figure 2 (top to bottom) shows the particle size distributions of the three kaolins investigated. It is evident that the sedimentation curves are always below the laser diffraction curves. This is a common finding which may be considered of general validity, irrespective of possible equipment-specific measurement errors. From the difference of the median values we obtain via Equation 8 the average aspect ratios 17.4, 17.7 and 22.3 for kaolins KDK, Imperial and SpEX, respectively. Figure 3 (top to bottom) shows the deflocculation curves, the minimum of these curves indicating optimum deflocculation. Based on these results, deflocculant concentrations of 0.3, 0.4 and 0.6 wt. % were used for preparing the suspensions of KDK, Imperial and SpEX, respectively. Figure 4 (top to bottom) shows the flow curves of optimally deflocculated kaolin suspensions in dependence of the solids content (kaolin volume fraction). Hysteresis (indicated by error bars) is generally small and the rheological character is close to Newtonian, except at the highest concentrations.

Figure 5 (top to bottom) shows the concentration dependences of the relative viscosities, and the fit curves obtained using the Krieger relation, Equation 9. The intrinsic viscosities obtained from the fit parameters are 12.8 ± 0.4, 7.1 ± 0.2 and 6.7 ± 0.1, extrapolated values of the critical volume fraction are 0.26 ± 0.02, 0.39 ± 0.01 and 0.56 ± 0.03, for suspensions of kaolins KDK, Imperial and SpEX, respectively.

Figure 6 shows the intrinsic viscosities determined for the three kaolins in comparison to the theoretical models available in the literature.

It is evident that the data determined with the method proposed lie within the Jeffery and Brenner bounds and that an average aspect ratio of 17–22 results in an intrinsic viscosity of 7–13, compared to 2.5 for spherical particles. However, unavoidable errors of measurement (in the aspect ratio determination as well as in the viscosity measurement) do not permit to seriously assess the influence of Brownian motion. Moreover, for such a precise assessment of this kind the width of the size distribution must be taken into account. Nevertheless,

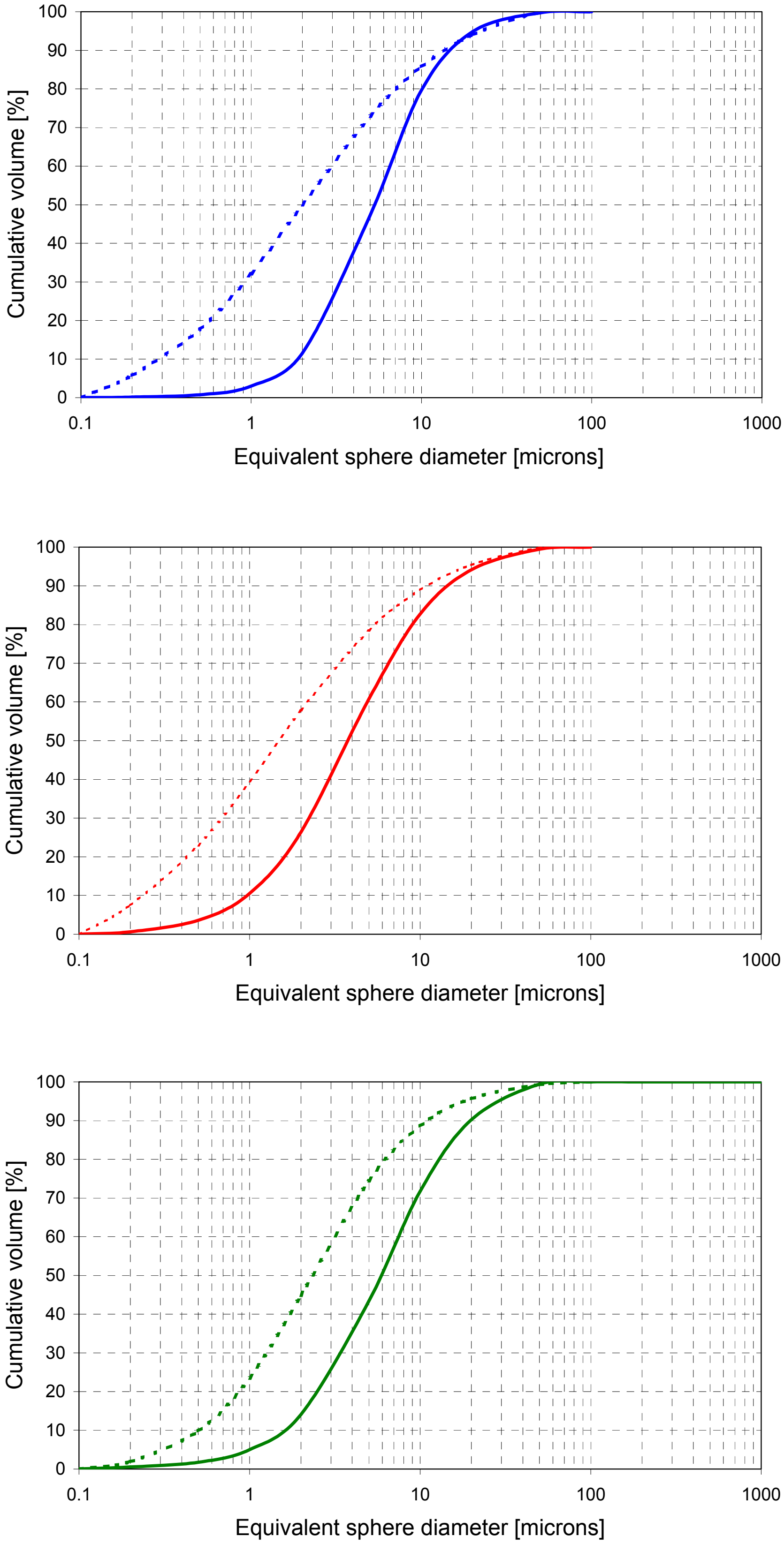

Fig. 2 Particle size distributions of kaolin KDK (top), Imperial (middle), and SpEX (bottom), measured by sedimentation (l.h.s., dotted curve) and laser diffraction (r.h.s., full curve).

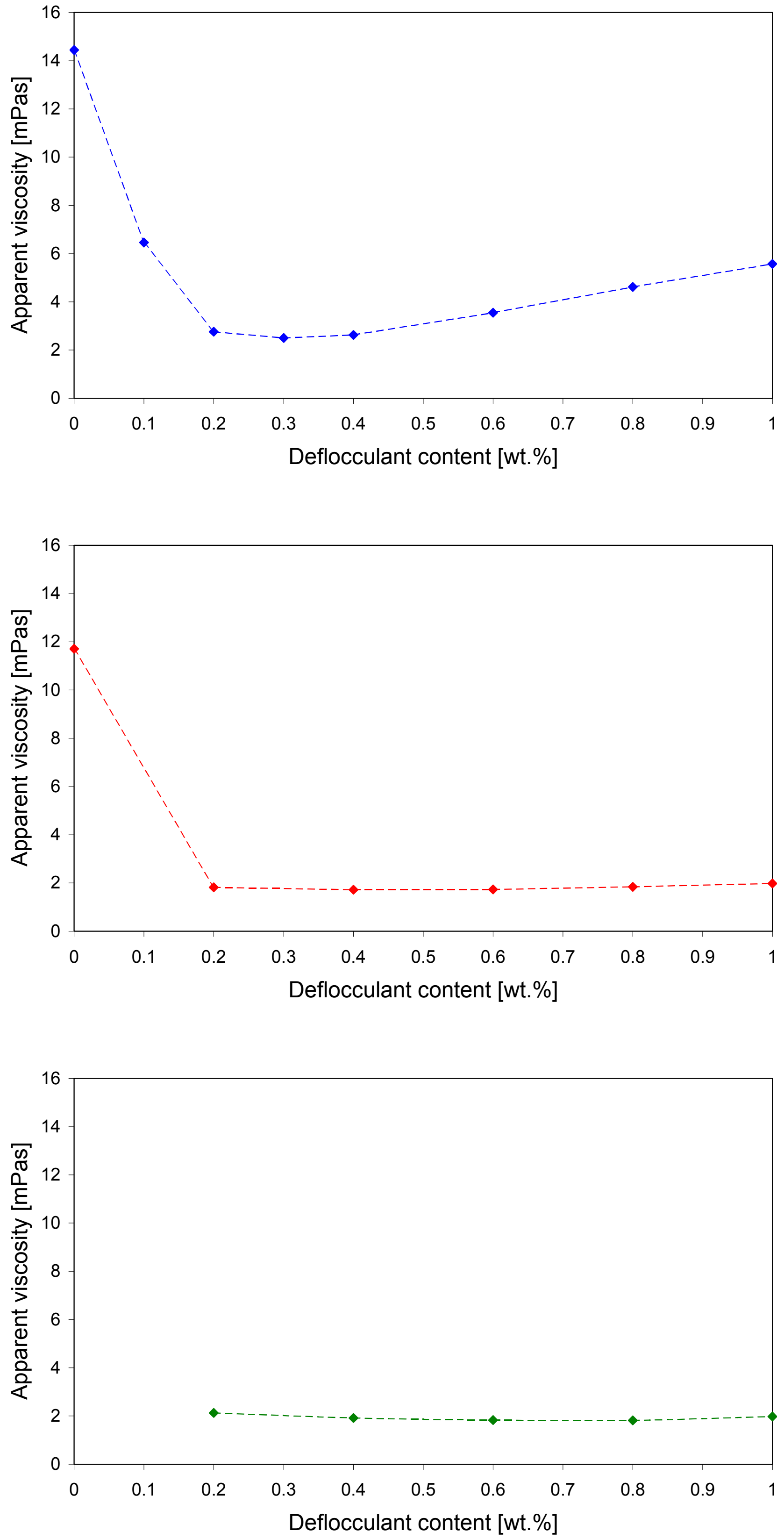

Fig. 3 Deflocculation curves of kaolin suspensions with 10 wt.% of kaolin KDK (top), Imperial (middle) and SpEX (bottom).

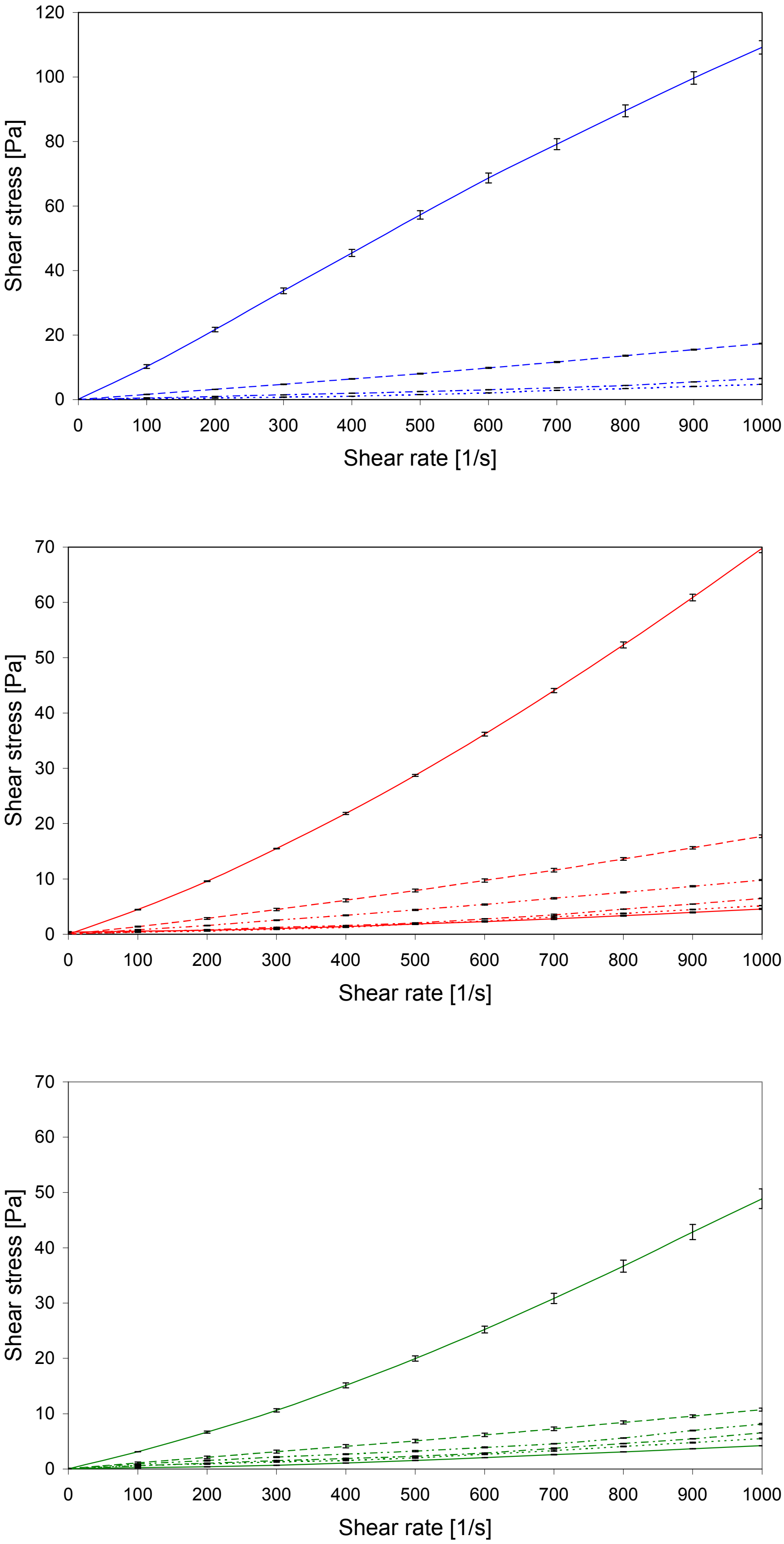

Fig. 4 Flow curves of kaolin suspensions KDK (top), Imperial (middle) and SpEX (bottom) with different kaolin contents (5-20 vol. %, 5-30 vol. % and 5-35 vol. % from bottom to top, respectively).

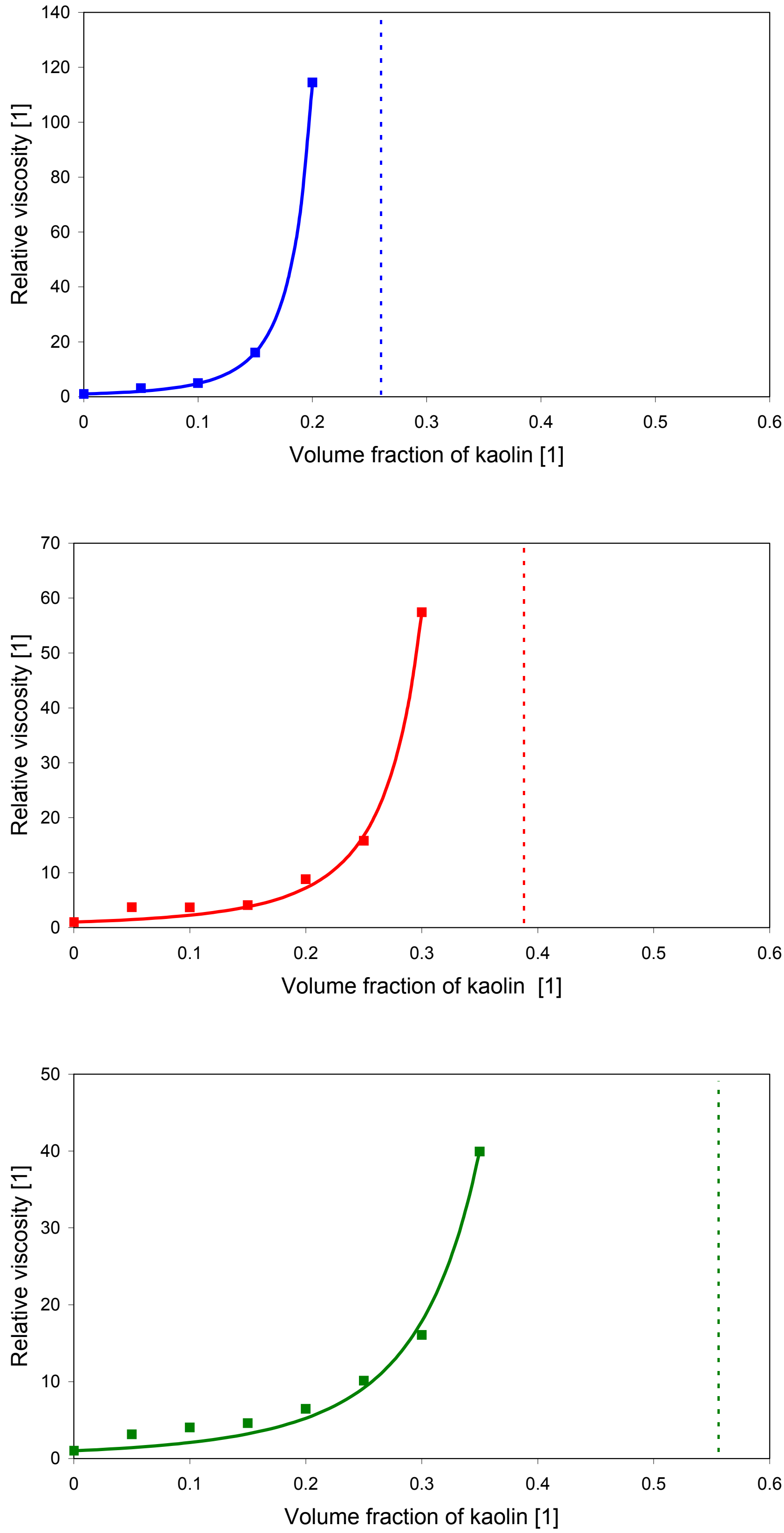

Fig. 5 Concentration dependences of the relative viscosity of kaolin KDK (top), Imperial (middle) and SpEX (bottom) suspensions (calculated from the apparent viscosity at a shear rate of 500 s^{-1}).

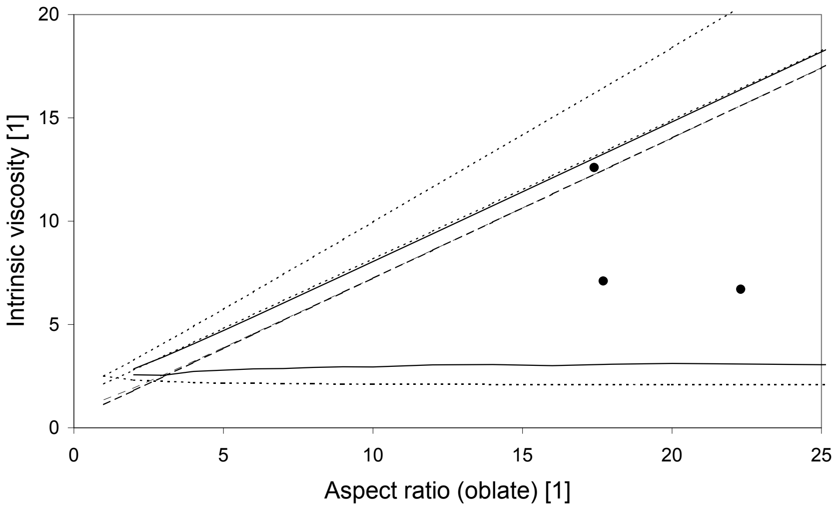

Fig. 6 Intrinsic viscosity versus aspect ratio; data points determined in this work (full circles), and Jeffery bounds (lowest and highest curves, dotted), Brenner bounds (full curves), Simha and Kuhn-Kuhn predictions (dotted and dashed, respectively – almost undistinguishable), as well as linear regression line of the Brenner upper bound and Scheraga's numerical data (dotted line – almost undistinguishable from the Brenner upper bound).

the method proposed here can principally be used to predict the intrinsic viscosity when the average aspect ratio of the system (and its average size) is known, and vice versa.

SUMMARY AND CONCLUSION

Based on the investigation of three Czech kaolins as paradigmatic examples, the influence of particle shape on suspension rheology has been discussed. The Brenner relation has been identified as the currently most widely recognized model equation relating the intrinsic viscosity to the aspect ratio. A useful linear approximation to the upper bound (dominant Brownian motion) has been proposed, $[\eta]_0 \approx 1.45 + 0.672 \cdot R$, and a recently proposed formula has been used to determine an average aspect ratio from a comparison of sedimentation and laser diffraction sizing data. The intrinsic viscosity has been obtained by a multistep procedure: firstly, flow curves were recorded for each kaolin with the optimum deflocculant concentration, secondly, the (apparent) relative viscosities read off from the flow curves were plotted against the kaolin volume fraction and, thirdly, these data were fitted using the Krieger relation to obtain the intrinsic viscosity in the asymptotic dilute limit. It has been shown that the data determined with the method proposed are within the Jeffery and Brenner bounds and that an average aspect ratio of about 20 results in an intrinsic viscosity of about 10, compared to 2.5 for spherical particles.

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