Chinese Materials Research Society

Progress in Natural Science: Materials International

ORIGINAL RESEARCH

Rheology of aqueous BeO suspension with NH$_4$PAA as a dispersant

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Abstract   The effects of dispersant amount and solids loading on rheological behaviors of aqueous BeO suspensions were investigated. The relationship of viscosity and solids loading determined experimentally was compared with five various existing models. BeO aqueous suspensions exhibited a shear dependent behavior from shear thinning to shear thickening with the increasing of shear rate. The rheological behaviors of the suspensions are in reasonable accord with the model proposed by Liu, and are basically consistent with the Dabak model and Chong model, but are discrepant to other two models proposed by Krieger–Dougherty and Kitano. The maximum solids loading is estimated to be 0.577.

1. Introduction

In the past decades, colloidal processing of ceramics combining advantages such as the microstructure homogeneity and the ability to form complex-shaped articles has been widely used for producing high-integrity ceramic components [1–6].

During the process of these suspension-based forming techniques, it is important to yield suitable suspensions with as high solids loading and low viscosity as possible. However, the suspensions with clusters and flocs always display a relatively high suspension viscosity due to the presence of attractive Van der Waals forces. Therefore, many dispersants referred to as polyelectrolytes are generally added into a suspending medium such as water to control the surface charge of the powders, for example, by the adsorption of charged polymers and achieve adequate dispersion of ceramic powders. Polyelectrolyte is a kind of polymer that possesses a charge that is present along the length of the polymer chain, as opposed to other polymers that have a charged species at one end of the molecule only [7,8]. These polymers used as dispersants are restricted to 'weak' polyelectrolytes such as polyacrylic acid (PAA),

polymethylacrylic acid (PMAA) and their (usually ammonium) salts [7] that are derived from the weak acid groups such as carboxylic acids.

The rheology of suspension is quite dependent on many factors. For example, it is easily affected by the dispersant amount in suspensions. Most significantly, the solids loading of suspensions also has a crucial effect on the rheological behavior due to adsorption of charged polyelectrolyte. In the general case, the viscosity of suspensions increases with increasing solids loading due to the reduction of the inter-particle distance. Hence, the relationship between suspension viscosity (η) and solids loading (Φ) has received much more attention for a long time, and has been the focus of many theoretical and experimental considerations for years. With the assumption of spherical, non-interacting rigid particles in a dilute solution, the first equation of Einstein [9] describing η–Φ behavior was proposed, and then a number of equations were rigorously proposed [10–14]. Although, for suspensions with highly concentrated solid fraction as commonly used in ceramic processing, the prediction of η–Φ relationship from the viscosity models aforementioned is much less accurate, the predictive capability has improved significantly for concentrated suspensions by taking the particle size distribution and most critically, the maximum solids loading (Φ_m) into account. In view of the literature, the value Φ_m is by far one of the most important parameters in describing the rheological properties of colloidal suspensions [8,10,15,16] as well as determining the inter-particle distance [8,17].

The objective of this work is to study the effects of dispersant amount and solids loading on the rheological behavior of BeO aqueous suspension. Besides, the relationship between relative viscosity (η_r) and solids loading (Φ) determined experimentally was compared with five various models to attain a complete understanding of the influence of solids loading.

2. Experimental procedure

Beryllia powder (Shuikoushan Nonferrous Metals Co., Ltd., Hunan, China) with a specific surface area of 4.16 m^2 g^{-1} (vendor specification) was used. A commercially available NH$_4$PAA (A-6114, Toagosei Chemical, Japan) was used as the

polyelectrolyte dispersant. Reagent-grade NaCl powder, and nitric acid (HNO$_3$) or ammonia (NH$_4$OH) solutions (Shanghai Chemical Reagent Co., Ltd., Shanghai, China) were also used; and the distilled water was produced in our laboratory.

In order to remove adsorbed water on the surface of BeO powder, the powder was dried at 120 °C in an oven for 24 h. Firstly, the NH$_4$PAA dispersant was mixed with distilled water using 2, 3, 4, 5 and 6 mg of NH$_4$PAA per gram of BeO (referred to henceforth as mg g^{-1}). And then, the BeO powder was mixed in the pre-mixtures with different values of Φ from 0.35 to 0.52. Finally, these powder mixtures were ball-mixed using 10 mm diameter high-purity zirconia balls in a high-density poly(ethylene) bottle of a certain volume for 24 h. The pH of the mixtures was adjusted by addition of reagent-grade HNO$_3$ or NH$_4$OH to predetermine pH from 3 to 9 in a way such that the addition of chemicals did not influence the overall solids loading.

Rheological behaviors of these aqueous suspensions were determined with the continuous shear mode increasing from 1 s^{-1} to 1000 s^{-1}. All measurements were performed at constant temperature (25 °C).

3. Results and discussion

3.1. Effect of dispersant amount on rheology of suspension

Fig. 1 illustrates the flow behavior of suspensions with different dispersant amounts over a shear rate range from 1 to 1000 s^{-1}. It shows that all the suspensions exhibit a shear thinning flow character in a low shear rates regime then followed by a shear thickening flow at higher shear rates. In the suspensions, particle agglomerations mainly resulting from the Van der Waals attractive potential between neighboring particles in the given liquid medium [18] may exist in the suspensions persistently. The agglomerations are broken down into smaller flow units as shear is applied. As shear rate increases further, suspension structure will tend to become more uniformly packed so that the resistance to flow reduces, resulting in the shear thinning phenomenon observed at low shear rates. When the shear rate approaches a certain critical point, the structure existing in suspension appears to be disrupted, leading to the shear thickening phenomenon. According to Barnes [19], the
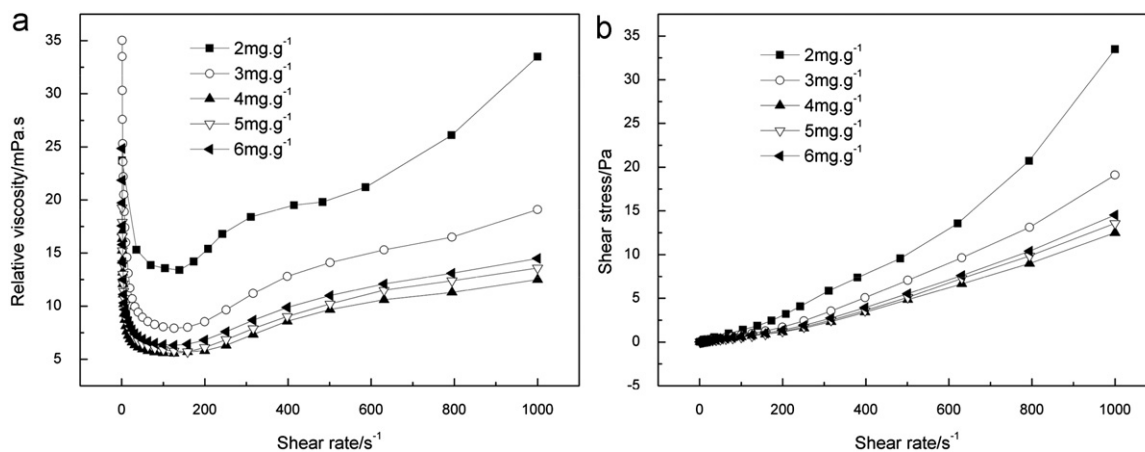

Fig. 1 Rheological flow curves of BeO suspensions with dispersant amount from 2 to 6 mg g^{-1}: (a) relative viscosity vs. shear rate and (b) shear stress vs. shear rate.

change of viscosity is due to the microstructure transition from a two-dimensional layered arrangement of particles to a random three-dimensional form. The original two-dimensional particle arrangement is caused by the flow itself rearranging the particles into closely placed sheets flowing over each other. This layered arrangement gives the lowest possible viscosity for a suspension. At higher shear rates, the hydrodynamic action that brought about this layering gradually disrupts. In addition, partial rod-like particles of powder as shown in Fig. 1 may play a promoting role in the conversion [20]. These particles can align along the flow direction. However, the formed alignment is easily disrupted, particularly at low shear rates [21].

It may also be observed from Fig. 1(b) that the slope of curves of shear stress vs. shear rate reduces initially and increases afterward with the increase of dispersant amount, and $4\,mg\,g^{-1}$ is the critical value. This indicates that flow resistance, corresponding to viscosity shown in Fig. 1(a), is affected by dispersant amount. With the addition of NH_4PAA, almost all the viscosities of suspensions with different pH values are declined firstly until the dispersant amount reaches about $4\,mg\,g^{-1}$, and then these values are increased. This could be attributed to enhancement of the zeta potentials of the powder due to the adsorption of NH_4PAA. The zeta potential of BeO powder with $4\,mg\,g^{-1}$ of dispersant, as shown in Fig. 3, increases up to $-25.3\,mV$, $-27.1\,mV$ and $-30.4\,mV$ at a pH of 6.0, 7.0 and 8.0, respectively. Consequently the electrostatic repulsion between particles is enhanced. In addition, the electrostatic repulsion between the charged carboxylate groups prevents the accumulation of groups at the surface, and the polyacrylate adsorbs in a stretched-out configuration, which results in long range steric interactions of NH_4PAA at the solid–liquid interface [7]. Thus, the steric interaction of the adsorbed polyacrylate has a positive contribution to the dispersion. The viscosity of suspension at pH 8 was reduced in that the particles are completely covered in the dispersant. For the amount of NH_4PAA in suspensions more than $4\,mg\,g^{-1}$, addition of dispersant increases the slope of curves of shear stress vs. shear rate due to excessive dispersant in solution. This increment could be attributed to interactions between the free polymers in the media. The polyelectrolyte exists in suspensions with 3 configurations: train, loop, and tail [7,22]. At a pH above the dissociation point of NH_4PAA (~pH 3.5, as mentioned before), the charged dispersant is adsorbed onto the particle surface with the configuration of tails mainly. Therefore, excessive polyelectrolyte with the configuration of tails in flowing suspensions is entangled with each other; the lubrication force must be increased. In addition, excessive polyelectrolyte increases the ionic strength, thereby resulting in the large compression of the double layer [23]. Consequently, the electrostatic interparticle repulsion reduces, and the slope of curves, corresponding to viscosity, increases.

3.2. Effect of solids loading on rheology of suspension

According to previous results, beryllia suspensions with 4 mg g^{-1} NH_4PAA at pH 8 were used to study the relationship between solids loading and viscosity. Fig. 2 illustrates the rheological flow curves for beryllia suspensions as a function of solids loading ranging from 0.35 to 0.50, over a shear rate range from 1 to $1000\,s^{-1}$. We can see that the rheology of
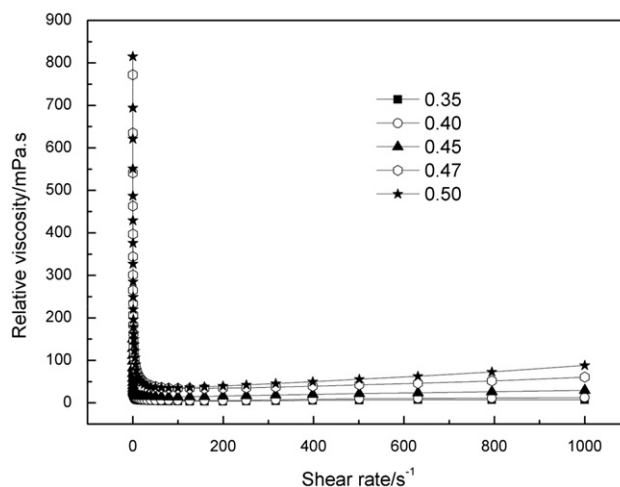

Fig. 2 Rheological flow curves of BeO suspensions as a function of solids loading.
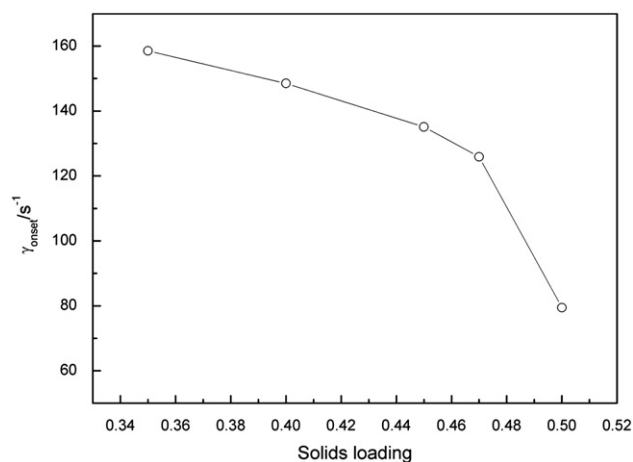

Fig. 3 Onset shear rate of shear thickening flow related to solids loading.

suspensions is a shear dependent behavior as shown in Fig. 1. Interestingly, it may be noted that the onset shear rate for shear thickening flow to occur seems to be related to solids loading. Define the corresponding shear rate at which the flow character changes as the critical shear rate for the shear thickening flow, γ_{onset}. The curves of critical shear rate (γ_{onset}) against solids loading (ϕ) from the data of Fig. 1 are given in Fig. 3.

The γ_{onset} seems to reduce as solids loading increases. According to Hoffman's theory [24,25], the shear thickening phenomenon is attributed to the order–disorder transition of the particle structure in suspensions. That is, the particles of their ordered layers break out at some critical level of shear rate and jam into one another, thereby causing the rise in viscosity. The average separation of particles reduces with increasing solids loading, so the probability of particles 'jamming' increases and the γ_{onset} reduces. Besides, it has also been found that the γ_{onset} is controlled by parameters such as particle shape, particle size, particle size distribution, particle–particle interaction and continuous phase viscosity (medium viscosity) [19]. Similar findings have been reported by many
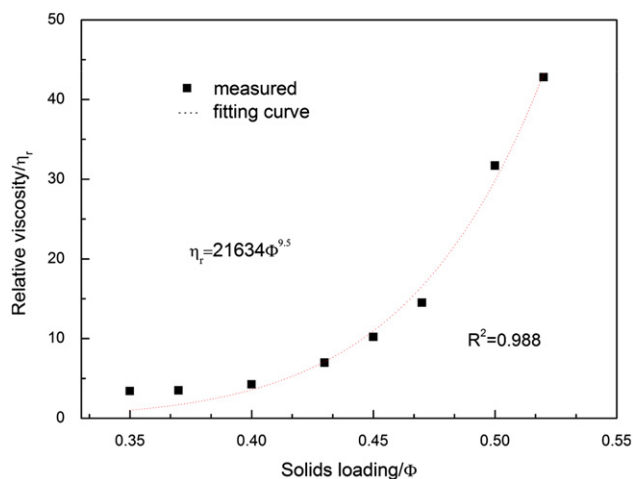
Fig. 4 Influence of the solids loading (Φ) on the relative viscosity (η_r) of suspensions with $4\,\mathrm{mg\,g^{-1}}$ NH$_4$PAA. The shear rate is $100\,\mathrm{s^{-1}}$.

Fig. 5 Determining maximum solids loading (Φ_m) from the $(1-\eta_r^{-1/2})-\Phi$ relationship.

researchers. However, a different result about the relationship between γ_{onset} and solids loading was reported by Tseng and Li [18] recently. In their study on nanosized BaTiO$_3$ suspension, the γ_{onset} increased with solids loading initially, reached a maximum at a critical level of solids loading, and then decreased as the solids loading further increased. It is regretful that the reason of this transition remains in dispute [18]. It is obvious that the relationship between the γ_{onset} and solids loading needs further research.

Fig. 4 shows the relationship between solids loadings (Φ) and relative equilibrium viscosities (η_r) of these suspensions at a shear rate of $100\,\mathrm{s^{-1}}$. η_r is defined as the ratio of suspension viscosity (η_s) to the viscosity of dispersant medium (η_o). It can be seen that the η_r is enhanced sharply with Φ in an exponential form: $\eta_r = 21,634\Phi^{9.5}$ (correlation factor $R^2 = 0.988$). The large coefficient and exponent value indicate that the viscosity of beryllia suspension is also strongly dependent on the volume fraction due to a decrease in the average separation distance between the particles with increasing volume fraction [23,26]. In addition, η_r shows an increase more pronouncedly as the solids loading exceeds about 0.4. The same phenomenon was also found in the BaTiO$_3$ suspension systems for $\Phi > \sim 0.4$ and in the TiO$_2$ suspension systems with nanoparticles for $\Phi > \sim 0.1$ by Tseng and Lin [23]. This suggests that the phenomenon is universal and there might be a certain critical value of Φ existing in all the high-solids loading suspensions unrelated with the kinds of system. The Van der Waals force, i.e., attractive force between particles increases with the solids loading Φ more quickly as Φ is above a certain value in that the inter-particle potential related with distance might be just at the second minimum value [27], resulting in a great improvement in the viscosity of suspension.

As shown in Fig. 4, there must be a maximum solids loading for a given suspension as the viscosity approaches infinity. A model proposed by Liu [10] has been used to estimate Φ_m in theory and proved to be suitable [18,26]. The Liu mode has a form of

$$1-\eta_r^{-1/n} = a\boldsymbol{\Phi} + b \qquad (1)$$

where a and b are constants, and n is a flow-dependent parameter also related to suspension property. According to
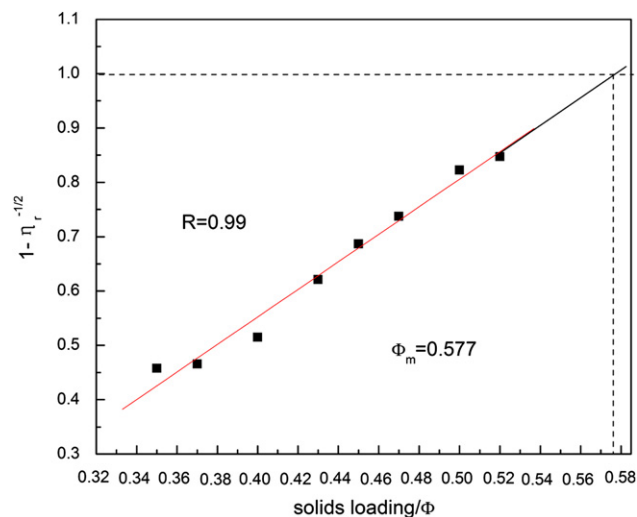
Liu [10] and Song's reports [26], the exponent n is taken as $n = 2$ since this value was reported to give a reasonable prediction of viscosity for suspensions at relatively high shear rates. Hence, maximum solids fraction (Φ_m) can be achieved from the linear relationship of $(1-\eta_r^{-1/2})$ with Φ.

As shown in Fig. 5, the experimentally determined $(1-\eta_r^{-1/2})$ values appear linearly proportional to Φ over a broad range of solids loading investigated ($\Phi = 0.35$–0.52). The correlation factor $R = 0.99$ indicates that the linear fitting is reasonable. Φ_m of the given suspensions was then determined as 0.577 by extrapolating the fitted linear line to $(1-\eta_r^{-1/2}) \to 1$. Compared with the random close packing of nanosized particles ($\Phi_m \sim 0.64$), the calculated value of Φ_m is lower as the same as the result of Tseng and Lin [23]. They attributed it to initially existing particle agglomeration in powders though after the high-shear ball mixing, or a porous, three-dimensional network of interconnected network (especially in suspension with nanoparticles). However, the experimental phenomenon of our beryllia system resulted presumably from the apparent shape of particles found in the starting powder (Fig. 1). The irregular shape increases the friction force between the particles. In addition, the theoretical volume fraction of the random close packing of nanosized particles is reduced for the same reason.

3.3. Models fitting the relationship between solids loading and viscosity

The relationship between solids loading and the viscosity of suspensions is very interesting and important in ceramic colloidal processing. Many researchers have taken great efforts to attain stable suspensions with high solids loading for reducing drying shrinkages and maintaining uniform particle packing, both of which are significant in achieving near-net shape forming. As illustrated in Fig. 4, a little variation in volume fraction can exert a pronounced influence on the viscosity of suspensions (especially with high solids loading). Therefore, many theoretical or empirical models have been proposed to ascertain the relationships between

solids loading and the viscosity. In the present study, five models are utilized to predict the increase of viscosity with the solids loading.

Among them, a well-known semiempirical Krieger–Dougherty equation [11] for uniform-sized colloidal suspension with spherical geometry of particles has the form

$$\eta_r = \left[1 - \frac{\Phi}{\Phi_m}\right]^{-[\eta]\Phi_m} \qquad (2)$$

where $[\eta]$ is the intrinsic viscosity, which is relevant to solids loading, immobilized liquid on particle surface, agglomerates, and dispersant medium [28]. Besides testing a wide variety of samples and fitting a curve, there is no way to directly measure the value of $[\eta]$ [28]. Among the fitting equations, it is a simple and reasonable method [18,29] to obtain the $[\eta]$ value from a linear fitting of $\ln(\eta_r) - \ln[1 - (\Phi/\Phi_m)]$ relationship, as shown in Fig. 6. So, according to our experimental results, the $[\eta]$ value is determined as 2.53, which is close to the calculated value of 2.5 by Einstein [9] for a dilute suspension of spherical particles.

The second one is the equation of Dabak and Yucel [12] which contains two changeable parameters $[\eta]$ and a term n. The model is given as

$$\eta_r = \left[1 + \frac{[\eta]\Phi\Phi_m}{n(\Phi_m - \Phi)}\right]^n \qquad (3)$$

where the value of n is taken as 2 at relatively high shear rates and will be used for data fitting in this study, since this value was reported to give a reasonable prediction of the viscosity of suspensions [10]. This equation is also solved with $[\eta] = 2.53$ as in Eq. (2).

The third one we used was developed by Chong et al. [13] in the form

$$\eta_r = \left[1 + 0.75\frac{\Phi}{\Phi_m - \Phi}\right]^2 \qquad (4)$$

The fourth model was proposed by Liu[10] to predict the viscosity of ceramic suspensions over a wide variety of materials. The equation has a more general form of
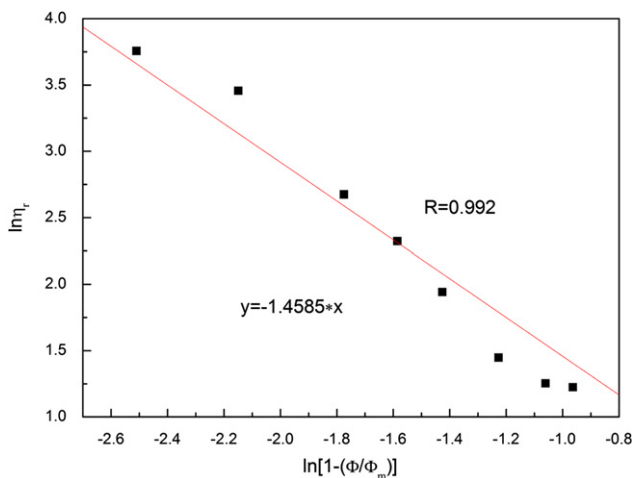
$$\eta_r = [a(\Phi_m - \Phi)]^{-n} \qquad (5)$$

where a is a constant related to Φ_m, and n is a parameter associated with flow and suspension property. Note that the term $(\Phi_m - \Phi)$ is just clearly defined as the effective space available for the particles to move in the matrix media. As $\Phi > \Phi_m$, the effective space reduces, and the viscosity of suspensions decreases and finally turns to be infinite at the point Φ_m. The value n is taken as 2 in that this value has shown a fairly good predictive ability in the model for many ceramic powder suspensions [26]. The value a can be obtained from a linear fitting of $(1 - \eta_r^{-1/2}) - \Phi$ plot (Fig. 5), and is determined as 2.534 from our experimental data of beryllia suspensions.

The last model we used, the empirical Kitano equation [14], was probably the best and simplest as claimed by a few researchers, with the very simple form

$$\eta_r = \left[1 - \frac{\Phi}{\Phi_m}\right]^{-2} \qquad (6)$$

Fig. 7 shows the comparison of the predicted η_r and the experimentally measured η_r. The number in this figure represents the solids loading of suspensions. The model proposed by Liu appears reasonable in predicting the relative viscosity over a large range of solids loading Φ for the effect of particle size and distribution and medium property when shearing conditions on viscosity of suspensions is neglected [12]. The predicted results of the Dabak model and Chong model are basically consistent with the experimental ones measured in the range $\Phi < 0.50$. However, large discrepancy between the measured result and the two residual models (Krieger–Dougherty and Kitano) are found almost in the whole range of Φ.

The discrepancy in the prediction found among the equations probably arises as a result of three reasons. The first one is the predictive nature and sensitivity of the equations. Unlike Liu's model, some effects, such as shape and distribution of the powders, surface chemistry of particle and the degree of dispersions (i.e. agglomerates and the carrier medium in suspension), are taken into account by the models corresponding to these equations [10,26]. In addition, all the models used assume implicitly a hard and same diameter sphere model in given suspension. However, as reported by Tseng and Li [18], the model should be treated as a suspension with 'soft' particles due to the fact that the polyelectrolyte used as
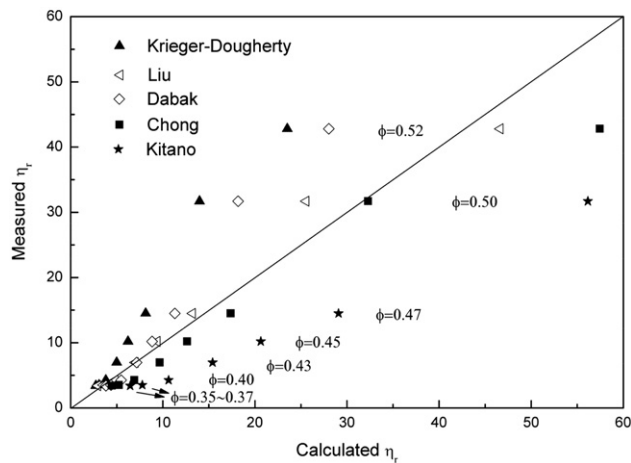

Fig. 6 Determining intrinsic viscosity $[\eta]$ from the $\ln(\eta_r) - \ln[1 - (\Phi/\Phi_m)]$ relationship of Eq. (2).

Fig. 7 Comparison of models calculated viscosity η_r with experimentally measured viscosity η_r.

dispersant existing in suspensions is adsorbed on the surface of particle and enlarges the effective radius. Hence, the Φ in all the equations should be replaced by the effective volume fraction of solids Φ_{eff} in the form [8,30]

$$\Phi_{eff} = \Phi \left(1 + \frac{\Delta}{a}\right)^3 \qquad (7)$$

where Δ is the thickness of the polymer layer, and a is the radius of the particle. The value of Δ ought to be obtained by precisely predicting the viscosity of suspensions. However, it has been reported that the adsorbed polymer layer is easily affected by many factors, such as configuration of polyelectrolyte, surface charge of the particle and so on. All of these are mainly dependent on the pH, dispersant amount, solids loading and ionic strength in suspensions as discussed in the above sections. Besides, the value of intrinsic viscosity $[\eta]$ used in the Krieger–Dougherty model and Dabak–Yucel model is also sensitive and changes as mentioned above. Noted that predictions of all the equations are more consistent with the experimental results of suspensions with lower solids loading. This might be due to the fact that the more dilute the suspensions are closer to the theoretical models.

4. Conclusions

The rheology of beryllia suspensions is a shear dependent behavior, shear thinning flow character at low shear rate and shear thickening flow at higher shear rate. The viscosity of suspensions decreased firstly and then increased with increasing of the concentration of dispersant in suspensions and 4 mg g^{-1} is a critical value. It increases with the increasing of solids loading (Φ) and is more pronounced as $\Phi > 0.4$. The reasons lie in the attractive force between particles which increases more quickly as Φ is above the critical value.

A maximum solids loading (Φ_m) was determined from the linear relationship of $(1 - \eta_r^{-1/2}) - \Phi$; from which, $\Phi_m = 0.577$, was attained for the given colloidal system. Five existing models have been used to predict the relative viscosity of the suspension. The rheological behavior of the suspension is in reasonable accordance with the model proposed by Liu over a wide range of $\Phi = 0.35–0.52$, is basically consistent with the Dabak model and Chong model in the range $\Phi < 0.50$, and was discrepant to two residual models (Krieger–Dougherty and Kitano).

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