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Studies on the rheological properties of aluminium oxihydroxide (boehmite) colloidal suspension

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Abstract

This paper presents both experimental and theoretical aspects of the rheological properties and gelling behavior of boehmite suspensions over a range of pH, temperature and concentration. Boehmite sol–gel behaved as a non-Newtonian shear thinning fluid with the increase in consistency index k at lower pH. The flow behavior index (n) representing the relative degree of shear thinning was influenced by pH. The power law theory was used to explain the k and n for gelling behavior and the limit of pseudoplasticity of the boehmite suspensions. It was also found that the variation of activation energy with pH had an appreciable effect on the viscosity of the suspensions. Further it was observed that the density of the suspensions was strongly pH-dependent, with a maximum density at pH 1. Hence, it can be concluded that the rheological properties of colloidal aluminium oxihydroxide (boehmite) suspensions are predominantly affected by the physico-chemical parameters.

Keywords: Boehmite; Rheology; Sol–gel; Non-Newtonian; Flow behavior index

1. Introduction

Colloidal processing of suspensions is an effective and reliable approach in the fabrication of the advanced ceramic products. Among the various powder-processing techniques, colloidal processing has been well recognized as one of the common approaches in the fabrication of advanced ceramics, primarily because of its advantages such as low cost and more reliable properties in the ceramics products [1]. Boehmite (AlOOH), a well known aluminium oxihydroxide, has important applications in the preparation of catalysts and catalyst support in petrochemical and petroleum refining processes [2]. It is also used as a starting material for the preparation of ceramic membranes and coatings [3].

Rheological investigations on colloidal suspensions or complex fluids help to understand the structural network and to characterize the interaction between the particles. It can also be an important tool to characterize sols and the sol–gel transition [4]. Cristiani et al. [5] and Tsai et al. [6] studied the effect of aging time on rheology of alumina slurries and Fauchadour et al. [7] studied the peptization mechanism of boehmite suspension. Song and Chung [8] studied the rheological properties of aluminium alkoxide in acid and basic solutions. In a similar approach, Moreno et al. [9] and Schilling et al. [10] studied the effect of additives on the rheology of alumina slurry. Despite several rheological studies on colloidal suspensions, there is little information on the rheological properties of boehmite suspensions as a function of process variables such as pH, temperature and concentration. Hence, an attempt has been made to investigate aforementioned properties in this work. The effects of the process variables on the rheological properties of colloidal boehmite suspensions were determined and correlated to the Oswald-De

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Waele power law model. The effect of pH on the suspension stability was also investigated by a sedimentation method.

2. Experimental

2.1. Preparation of boehmite suspension

Boehmite (AlOOH) powder was provided by BASF chemical company (G-250, medium density (505 kg/m^3) pseudo-boehmite alumina, BASF Catalysts LLC in USA, purity > 99%). The concentrated hydrochloric acid (JT Baker, Mexico) was used. The boehmite powder was mixed with deionized water at different concentrations ranging from 5% to 30% (w/v). The suspensions were dispersed by sonication for 2 min. For sonication, a microprocessor based and programmable ultrasound processor was used (Autotune series, model 750 W). This processor had a frequency of 20 kHz with maximum power output of 750 W. In addition, the processor had the facilities of amplitude controller, which was set at 70% during experiments. Subsequently, the suspensions were stirred by a mechanical stirrer for a period of 20 min at a speed of 150 rpm. The suspensions were then left unperturbed for an additional 30 min for removal of air bubbles and better homogeneity, which is essential prior to the rheological measurements. The suspensions were further acidified to different pH (1.0–7.6) at 25 °C by the addition of concentrated hydrochloric acid. Then suspensions were evaluated with respect to their rheology by means of viscosity measurements.

2.2. Measurement of boehmite particle size

A dynamic laser diffraction particle size distribution analyzer (HORIBA; LA-300) was used to measure the size distributions of the boehmite particles. The suspension was prepared by dispersing the powders in distilled water at a constant temperature of 25 °C. The suspension was then treated to ultrasonic vibrations for 3 min to de-clump the clusters. This equipment is operated through the LA-300 software package that performs all the functions, such as making measurements, storing and retrieving data, etc. The LA-300 software automatically calculates the particle size distribution.

2.3. Measurement of density of boehmite suspensions

The liquid density was measured at 25 °C using a digital density meter (DA-110M, Kyoto Electronics Manufacturing Co. Ltd., Japan). The liquid was manually pumped through a tube into a density meter and a stable reading of density was recorded.

2.4. Measurement of pH of boehmite suspensions

The pH of the liquid was measured by a pH meter at 25 °C (Cyber Scan pH 1500, Eutech Instruments Pte Ltd., Singapore). The pH of the prepared aqueous suspensions of boehmite was constant at 7.6 for all concentrations. With addition of concentrated hydrochloric acid, the pH changed from 7.6 to 1.

2.5. Measurement of rheological properties of boehmite suspensions

The rheological properties of the boehmite suspensions were determined using a rheometer (Programmable DV III+ Rheometer, Brookfield Engineering Laboratories, Inc., USA). The appropriate disc spindles HA/HB-2, HA/HB-3 were used for viscosity measurement at zero shear rate, whereas the spindles SC4-18 and SC4-28 were used for viscosity measurements at different shear rates. The rheometer was calibrated with the standard fluids each time before it is used. The rheometer was connected to a circulating water bath (Brookfield Refrigerated Bath/Circulator Model TC-500, Brookfield Engineering Laboratories, Inc., USA) to control the suspension temperature from 25 to 75 °C. The flow curves (shear stress versus shear rate, viscosity versus shear rate) were determined at shear rates in the range between 10 and 300 s^{-1}. For the sample was allowed to rest for 3 min between loading and measurement. Triplicate measurements were made for each sample.

2.6. Determination of consistency index (k) and flow behavior index (n)

The effect of different pH on the viscosity of suspensions was investigated by using the Oswald-De Waele model given by Eq. (1), also known as the power-law model [11].

$$\tau = k(\gamma)^n \tag{1}$$

where τ is the shear stress in dyne per cm^2, γ is the shear rate per second (s^{-1}), k is the consistency index (Pa s) and n is the flow behavior index. Eq. (1) can be transformed to the log-linearized form as follows:

$$\log \tau = n \log \gamma + \log k \tag{2}$$

By plotting the experimental data in the form of log τ versus log γ, a straight line can be obtained; by linear regression the straight line intercept k, and slope, n, can be evaluated. The n is a measure of the deviation of the fluid from Newtonian behavior. If $n=1$ then this expression simplifies to the Newtonian definition. When n is less than 1, it indicates the degree of ‘shear thinning’-the reduction in viscosity as shear rate increases. If the value of n is greater than 1, the opposite behavior-increasing viscosity with increasing shear rate is also known as ‘shear thickening’.

2.7. Determination of activation energy for viscous flow

The effect of temperature on viscosity was evaluated and the activation energy for viscous flow (ΔE_η) [12] was determined by

$$\eta = A \exp(\Delta E_\eta / RT) \tag{3}$$

where η is the zero shear rate viscosity of the suspension, A is the temperature-independent pre-exponential factor, R is the gas

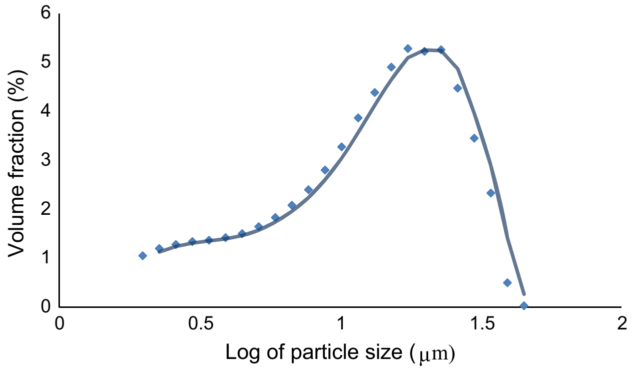

Fig. 1. The particle size distribution of boehmite powder after sonication.

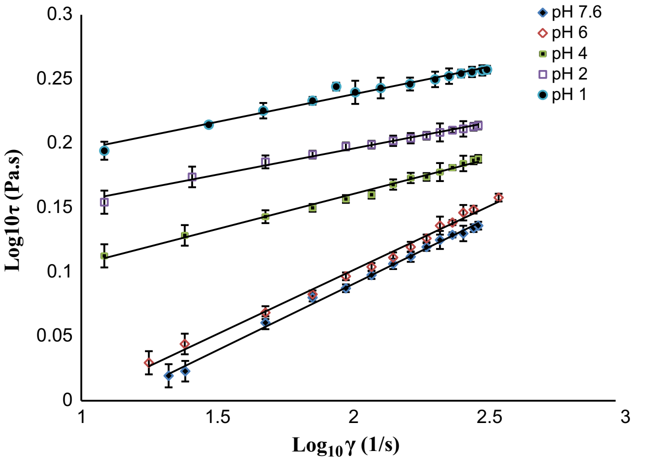

Fig. 3. Power law plots for the log shear rate (log γ) versus log shear stress (log τ) for pH range from 1.0 to 7.6 at 30% (w/v) of boehmite suspension at 25 °C.

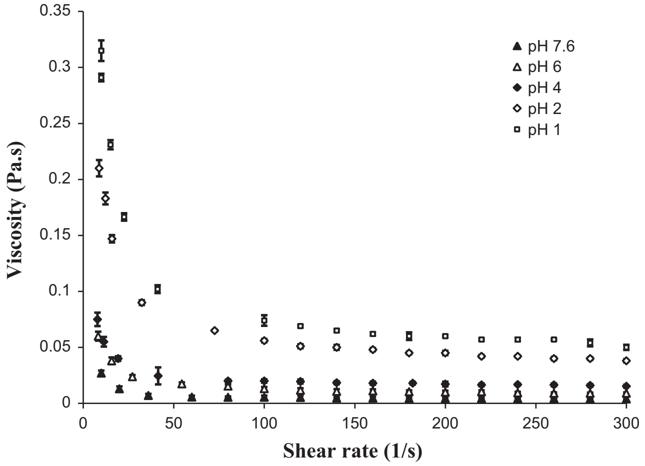

Fig. 2. Effect of shear rate on viscosity of 30% (w/v) boehmite suspensions for different pH at 25 °C.

constant (8.314 J/mol K) and T is the reaction temperature in Kelvin. Eq. (3) can be linearized into the following forms:

$$\log \eta = \log A + \Delta E_{\eta}/R(1/T) \tag{4}$$

The plot of log η versus $1/T$ should be linear with a slope equal to $\Delta E_{\eta}/R$. By linear regression, activation energy for viscous flow (ΔE_{η}) was evaluated.

3. Results and discussion

3.1. Rheological study of the suspension

The boehmite particles of the order of micrometers (Fig. 1) were suspended in deionized water at different concentrations (5–30% w/v). The gelling, as well as the rheological behavior of the boehmite suspension was determined with respect to the pH of boehmite suspensions. Fig. 2 presents typical flow curves for the boehmite suspension at different pH values. The viscosity decreased when the shear rate is increased from 10 to 100 s^{-1}, thus confirming the pseudoplastic behavior of the suspensions. This can be explained by the fact that the association between particles is formed after lowering the pH and the breaking up of those aggregates at high shear rates indicating shear thinning behavior. The results showed that the region of high shears rates (100–300 s^{-1}) where the viscosity is nearly independent with the shear rate. The viscosity in this region attains the Newtonian behavior for the suspensions. These results are in agreement with the results of Song and Chung [8], that the structure oriented by high shear rate could not return to its initial structure and thus the structure of the suspension remained constant over a range of shear rate (100–300 s^{-1}).

The power law model was found to give a close fit to the experimental data (Fig. 3) with correlation coefficient (R) values greater than 0.99 (Table 1). The low n values obtained from the low pH suspensions represent a significant departure from Newtonian flow behavior and these suspensions have high viscosities at low shear rates that decrease dramatically as the shear is increased. These relatively low n values indicate either a continuous breakdown or a realignment of the molecules of the suspensions along the direction of flow [13]. Moreover, these phenomena are characteristic of fluids rarefied by shear in which the suspension with high viscosity becomes less viscous or less dense due to the straightening molecules along the flow direction during the action of shear stress, causing the liquid to assume a more non-Newtonian character. The consistency index k increased with decreasing pH of suspensions. The high value of k is mainly attributed to the growing intermolecular friction forces and interactions. Moreover, the net charge of boehmite molecules at low pH may cause an expansion of the boehmite molecules, accompanied with higher hydration and swelling that may increase the value of k. Furthermore, the correlation between the rheological parameters k and n demonstrates that these parameters showed no consistent trend with pH and concentration.

3.2. The effect of temperature on viscosity and flow activation energy

Fig. 4 plots the natural logarithm of the apparent viscosity against the reciprocal of the absolute temperature (K). The activation energy of the flow processes was calculated according

Table 1
The flow characteristics parameter estimated from the shear rate and shear stress data of 30% (w/v) boehmite suspension.

pH	K (Pa s)	n	R^2
1.0	2.978	0.398	0.992
2.0	1.432	0.443	0.987
4.0	0.414	0.494	0.992
6.0	0.010	0.988	0.993
7.6	0.007	0.994	0.996

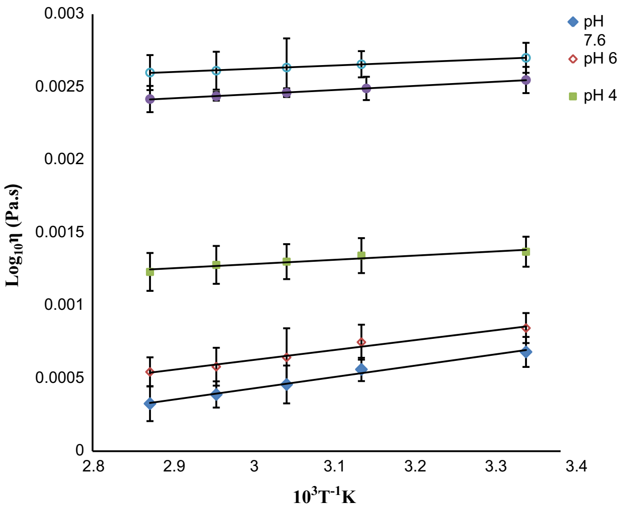

Fig. 4. Viscosity of boehmite suspension of 30% (w/v) at different pH as a function of temperature.

Table 2
Influence of pH on gelation at various temperatures of 30% (w/v) boehmite suspensions.

pH	Activation energy (ΔE) (J/mol)	R^2
1	13.41	0.989
2	11.88	0.981
4	6.71	0.987
6	5.69	0.994
7.6	5.47	0.989

to Eq. (3), and the results are summarized in Table 2. Temperature was found to have a considerable effect on the viscosities of boehmite suspensions, with a general tendency of decreasing viscosity with increasing temperature. The activation energy of colloidal suspensions correlated with the energy required for breaking the chemical bonds which facilitates faster flow, as reported by Poulain et al. [14]. The flow activation energy (ΔE) of the boehmite suspension was varied from 13.41 J/mol at pH 1 to 5.47 J/mol at pH 7.6 (Table 2). The higher values of ΔE of the sample at low pH can be explained in terms of an increase in the interparticle attraction forces between particles that tend to draw the particles together. The lower values of ΔE at high pH can be interpreted by the weak attractive forces between boehmite particles at higher pH. These results are also in agreement with previously published studies [15] that showed a similar temperature and pH dependency.

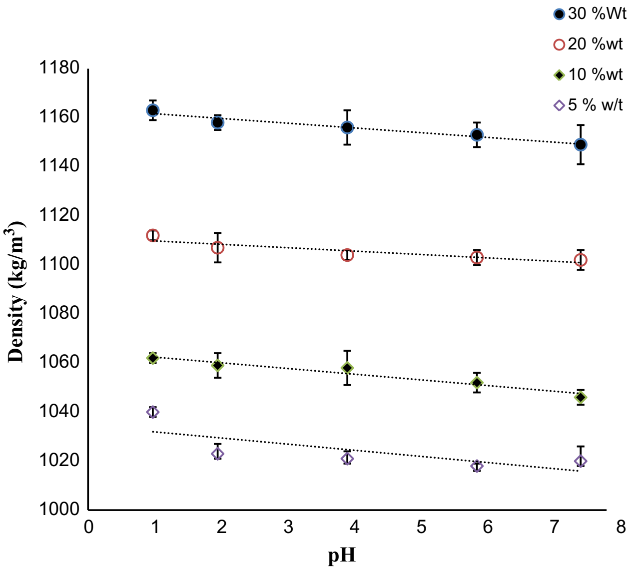

Fig. 5. Effect of pH on the density of different concentrations of boehmite suspensions at 25 °C.

3.3. Effect of pH on density

The pH of the boehmite suspension also affects the density of the boehmite suspensions as shown in Fig. 5. The difference in density was more robust in suspensions with higher boehmite concentrations. The boehmite gel density has been reported to vary as a function of pH due to the precipitation to the agglomerate state [16]. Besides, the formation of agglomerates due to the weak forces of attraction at lower pH, as described in earlier section attributed to the higher density of the boehmite suspension. On the other hand, the agglomeration may cause cross-linking between particles at lower pH, these chain may lead to fairly rigid structures which results in higher density of the suspension. Thus, it can be inferred that the density of the boehmite suspensions was varied depending on pH, with basic suspensions having a lower density than acidic suspensions.

4. Conclusions

The rheological properties of boehmite under controlled pH conditions showed a non-Newtonian pseudoplastic behavior. The suspensions with the high pH showed high sensitivity to temperature with low activation energy. At low pH, the density of the boehmite gel increased. Hence, it can be concluded that the physico-chemical parameters such as pH, temperature, density and concentrations have significant influence on rheology of the colloidal aluminium oxihydroxide (boehmite) suspensions.

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