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Rheological properties of boehmite sols during ageing at room temperature (30 ± 1°C) under closed condition

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Abstract. Boehmite sols were obtained by peptizing boehmite precipitates with glacial acetic acid. The sols were aged at room temperature (30 ± 1°C) under closed condition. Rheological properties of the sols were studied at different ageing times. The sol characteristics were interpreted by measuring their viscosity, areas of hysteresis of the flow curves and yield stress (τ_y). Viscosity and the area of hysteresis of the flow curves increased with increasing ageing time of the sols. A sharp change of yield stress was observed during the ageing period from 15 to 36 days. The change in viscous to elastic nature and the appearance of gel point of the sol was observed by studying their oscillatory flow behaviour, i.e. by measuring loss modulus (G''), elastic modulus (G'), and loss tangent ($\tan \delta$) of the sols. Gel point of boehmite sol was found at 36 days of ageing under closed condition at room temperature (30 ± 1°C).

Keywords. Boehmite sol; rheology; shear thinning; yield stress; viscoelasticity; gel point.

1. Introduction

Rheological behaviour can be an important tool to characterize sols and the sol–gel transition (Gonzalez *et al* 1992). Kozuka *et al* (1987, 1988) and Sakka and Kozuka (1988) studied the rheology of silica sols, and the sol–gel transition was rheologically studied by Sacks and Sheu (1987). Song and Chung (1989) studied the rheological properties of aluminium alkoxide in acid and basic solutions; however, not much information has been reported on the rheological properties of boehmite sols prepared from inorganic precursors. Boehmite sols find wide applications as precursor materials for the preparation of alumina and alumina-based powders (Ganguli and Chatterjee 1997), abrasives (US Patent 1986) etc and rheological studies of the same sol is becoming increasingly important to optimize the process parameters for the preparation of the above materials.

Boehmite sol can be obtained by the widely used Yoldas (1975a) method after peptization of aluminium monohydroxides formed by the hydrolysis of aluminium alkoxide at 75°C. Yoldas (1975a) showed the effect of different acids on peptization of boehmite particles; for better peptization the acid used should have an anion non-complexing with aluminium and it should have sufficient strength to produce the required charge effect at low concentrations. The type of acids used played a more important role rather than the pH of the system. In the present investigation acetic acid was chosen as the peptizing agent of boehmite precipitate. Precipitated boehmite particles were generally highly agglomerated (Chatterjee *et al* 1998); during peptization with acetic acid, the particles were broken down to 200–250 Å, producing a semi-transparent sol. In the as-prepared sol individual boehmite particles were surrounded by H^+ ions which were the product of dissociation of acetic acid. As acetic acid is a weak acid its dissociation power is weak (pKa = 4·76) generating relatively small number of H^+ ions required for adsorption on the surface of boehmite particles. At the same time the positively charged boehmite surface could adsorb the counter ions (acetate ions) which neutralized the surface charge effecting in decreasing the interparticle repulsion (Yoldas 1975b). Hence, during ageing the particles tended to come closer due to weak forces (e.g. polar, van der Waals forces). The attractive force became predominant over the repulsive forces and the sol was no longer stable. The weak forces of attraction between boehmite particles related to the flow behaviour of boehmite sols can be interpreted by rheological properties during their ageing.

The objective of the present investigation was (i) to study the nature of flow properties of the boehmite sols during their ageing with the help of steady shear flow behaviours and (ii) to identify the gel point during sol–gel transition of boehmite sols with the help of oscillatory flow behaviours.

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2. Experimental

2.1 *Preparation of boehmite sols*

For the preparation of boehmite sols, aluminium nitrate, $Al(NO_3)_3 \cdot 9H_2O$ (Extrapure, S.D. Fine-Chem Pvt. Ltd., purity > 98%) was used as the starting material. Boehmite particles were precipitated from the aluminium nitrate solution (0·55 M) at 85–90°C with an ammonia solution (3·5 M) at pH 7–8 as described earlier (Chatterjee *et al* 1998). The precipitate was washed with double distilled, deionized water (sp. conductance = 1.5×10^{-5} S sec^{-1}) to remove the electrolytes. The washed precipitate was peptized under vigorous stirring at 80°C with a minimum amount of acetic acid (99% glacial, Extrapure, S.D. Fine-Chem Pvt. Ltd.). An almost transparent sol was obtained after peptization within a period of 1 h at 80°C. The peptization was carried out in a closed container to avoid evaporation of the solvent molecules. The pH of the sol was measured as 5·07 at 30°C. The sol prepared as above was divided into several parts, 25 ml each in a 50 ml glass beaker. They were kept tightly closed covering the mouth of the beakers with polythene sheets and aged at room temperature (30 ± 1°C) for several days.

2.2 *Rheological measurements*

The rheological measurements of the boehmite sols were carried out by using a Haake rheometer (Rotovisco, model RT20) at 30°C. For this purpose, the rheometer was connected to a Haake heating bath (model K20) and a Haake circulator (model DC5). The instrument was connected to a computer loaded with Haake software (version V3). A cone/plate sensor (c60/1°) was used for all measurements.

Steady shear flow measurements of the samples in controlled rate (CR) mode were carried out by increasing the shear rate from zero to 1000 s^{-1} in 2 min followed by an immediate decrease in the shear rate from 1000 s^{-1} back to zero in another 2 min. The non-Newtonian nature of the flow curves of the respective sols was studied by measuring the area (Schramm 1995) of hysteresis ('up' flow curve area minus 'down' flow curve area). For the evaluation of the yield stress (τ_y), the Casson (1959) model was employed, which has the form

$$\sqrt{\tau} = \sqrt{\tau_y} + K\sqrt{\dot{\gamma}}, \tag{1}$$

where τ is the shear stress, τ_y the yield stress, K the constant, $\dot{\gamma}$ the shear rate. By plotting square root of shear stress ($\tau^{1/2}$) against square root of shear rate ($\dot{\gamma}^{1/2}$), a straight line was obtained. Yield stress (τ_y) was determined from the intercept of the straight line extrapolated at zero shear rate (Kwon *et al* 1997).

For oscillating testing of the sols and gels a sinusoidal shearing stress, (τ) was applied to the sol, which is a sine function according to the following equation (Schramm 1995)

$$\tau = \tau_0 \sin\omega t, \tag{2}$$

where τ_0 is the shear stress amplitude, t the time, ω the angular velocity. The resulting deformation (γ) developed in the sol can be represented by

$$\gamma = \gamma_0 \sin(\omega t + \delta), \tag{3}$$

where γ_0 is the strain amplitude, δ the phase displacement angle between applied stress and resulting deformation. The value of δ was a measure of the viscoelastic property of a sol. A purely viscous behaviour of the sol was obtained when stress signal was out of phase with strain signal ($\delta = 90°$); on the other hand, a purely elastic nature of the sol was shown by in-phase alignment of the stress and strain signals ($\delta = 0°$). A purely viscoelastic character of the sol and hence sol–gel transition i.e. the gel point, could be obtained when the stress and strain signals were in between in-phase and out-phase alignment ($\delta = 45°$). Schematically it is shown in figure 1. The complex modulus, G^*, can be calculated as

$$|G^*| = |\tau_0| / |\gamma_0|. \tag{4}$$

The complex stress modulus can be divided into viscous (loss), G'' and elastic (storage), G' moduli as follows

$$G'' = G^* \sin\delta, \tag{5}$$

$$G' = G^* \cos\delta. \tag{6}$$

The determined loss modulus (G'') was a measure of energy dissipated as heat during flow while the storage modulus (G') was a measure of energy stored elastically in the system after a shear perturbation (Kiratzis and

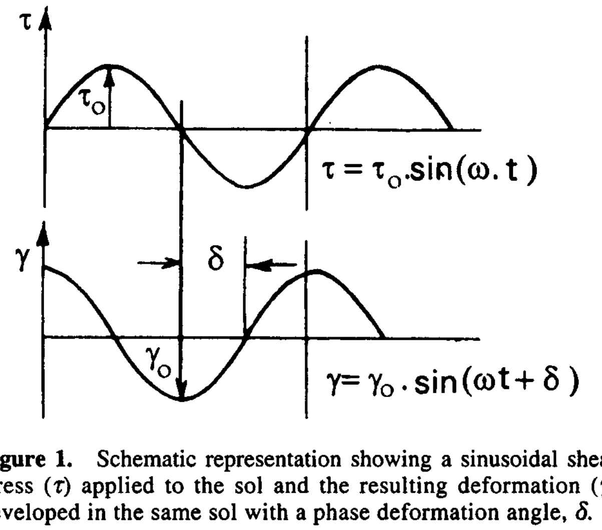

Figure 1. Schematic representation showing a sinusoidal shear stress (τ) applied to the sol and the resulting deformation (γ) developed in the same sol with a phase deformation angle, δ.

Luckham 1998). The dynamic flow behaviour i.e. loss modulus (G''), and storage modulus (G'), of the sols and gels was determined using oscillatory flow with a radial frequency (ω) of 0·924 rad s^{-1}. Loss tangent (tan δ) can be obtained from (5) and (6) as follows

$$\tan \delta = G''/G'. \qquad (7)$$

From the values of G'', G' and tan δ, the nature of the sol and the sol–gel transition (gel point) could be obtained.

3. Results and discussion

The changes of flow behaviour of the sols were observed at different time intervals. Figure 2 shows that viscosity (at the shear rate of 100 s^{-1}) increased with ageing time, the increase was more sharp after 15 days of ageing; however, it became less sharp after 36 days of ageing. For the sol obtained at the ageing time of 36 days, the changes of shear stress and viscosity with increasing shear rate is shown in figure 3 as an example. It shows that with increasing shear rate, the shear stress increased and viscosity decreased. The change of shear stress with shear rate made a hysteresis loop with 'up' flow and 'down' flow curves (figure 3). The change in the area of hysteresis obtained from the flow curves at different ageing times is indicated in figure 4. The area of the hysteresis loop became larger with increasing ageing time.

The aggregation of sol particles took place by weak forces (e.g. van der Waals forces etc) with ageing time (Song and Chung 1989). While a shear rate was applied to the sols, the entrapped liquid surrounding the sol particles was perturbed. As a result the individual sol particles oriented themselves in the direction of flow by breaking the weak forces of attraction of the agglomerate particles. This resulted in a decrease in viscosity with increasing shear rate (figure 3) showing shear thinning flow behaviour. On the other hand on decreasing the shear rate from higher range (1000 s^{-1}) to lower range (0 s^{-1}) the deagglomerated particles could not adhere to each other to the fullest extent during the time period over which the shear rate was decreased (figure 3). Moreover with increase in the area of hysteresis developed (figure 4) in the flow curves (shear stress–shear rate) the shear thinning of the sols increased. Thus the shear thinning behaviour of the sols could be a measure of the area of hysteresis of the flow curve. The area of hysteresis signifies the energy required to break down the aggregates. It is clear that aggregation of boehmite particles took place rapidly after 15 days of ageing as observed by their sharp increases in viscosity (figure 2) and area of hysteresis (figure 4) with ageing time.

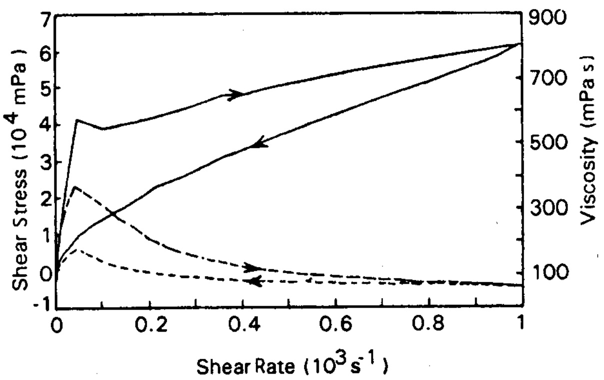

Figure 3. Changes of shear stress (——) and viscosity (- - -) with shear rate of the sol after 36 days of ageing at 30°C.

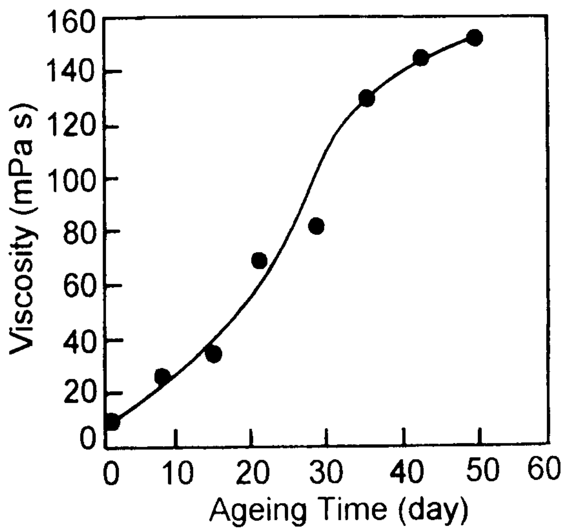

Figure 2. Change of viscosity (at the shear rate, 100 s^{-1}) of the sols with ageing time.

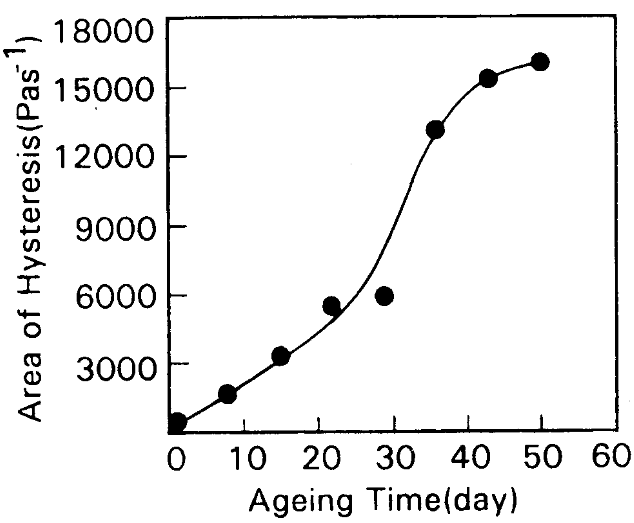

Figure 4. Plots of area of hysteresis of the flow curves vs ageing time of the sol.

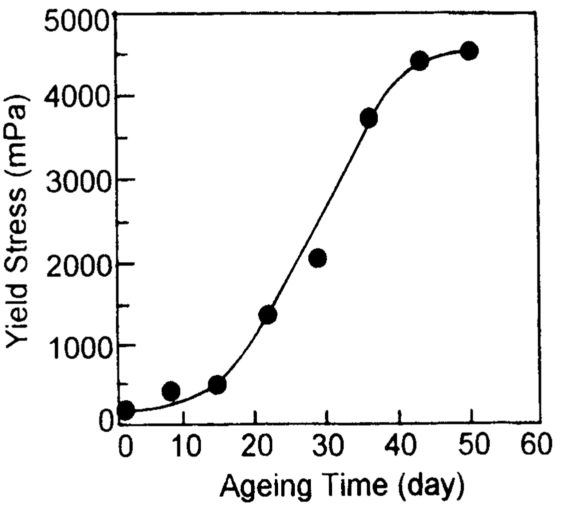

Figure 5. Change of yield stress with ageing time of the sol.

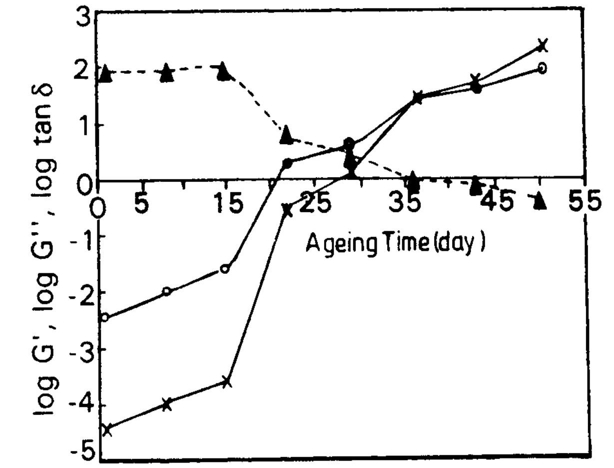

Figure 6. Plots of loss modulus, G'' (o), storage modulus, G' (×) and loss tangent, tan δ (▲) vs ageing time of the sol.

The measured flow curves were best fitted with Casson (1959) model. In this case the measuring points were considered from 'down' curves because they were smooth and had good reproducibility (Guo *et al* 1998). The yield values (τ_y) were plotted against ageing time in figure 5. It shows that yield stress increased slowly up to 15 days of ageing followed by its sharp rise up to 36 days of ageing. After 36 days of ageing a slow increase of yield stress was observed with increasing ageing time. The yield stress is the maximum stress which can be applied without destroying the aggregate particles (Drouin *et al* 1988); it should therefore be proportional to the strength of aggregates (Song and Chung 1989).

The structural changes that occurred in boehmite sols can be well understood by measuring their viscoelastic properties during sol–gel ageing period. Plots of loss modulus (G''), storage modulus (G') and loss tangent (tan δ) vs ageing time of the sol are shown in figure 6. It indicates that up to 15 days of ageing a steady change of G'' and G' occurred with ageing time, while tan δ shows practically no change. After 15 days of ageing the values of G'' and G' increased and tan δ decreased sharply up to 36 days of ageing followed by the slow increase of G'' and G' and slight decrease of tan δ up to 50 days of ageing. While the sol particles tended to come closer, more energy was required to break down the agglomerated particles by applying stress. The loss modulus (G'') which is a measure of energy lost as heat in friction between the agglomerated particles (Kiratzis and Luckham 1998), increased. At the same time, the storage modulus (G') which is a measure of energy stored elastically during the formation of elastic bonds between the sol particles, increased. In the viscous region ($\delta \sim 90°$), G'' was larger than G'; while the reverse was the case in the elastic region ($\delta \sim 0°$) (figure 6). The cross-over points of G'' and G' obtained at 36 days of ageing indicated the point of sol to gel transition i.e. gel point (Sacks and Sheu 1987). The gel point could also be proved from the tan δ curve touching on the time axis. At this point (36 days of ageing) the value, δ, became 45°; it pointed out the purely viscoelastic character of the boehmite sol. While the particle–particle interconnectivities were not evident in the sols, the applied shear stress and the resulting deformation (shear strain) remained out of phase (phase angle, $\delta = 90°$). It facilitated the fluidity of the sol. During the course of ageing particle–particle network structure was developed, and a viscoelastic nature ($\delta = 45°$) followed by an elastic network (applied stress and resulting strain were in-phase, $\delta = 0°$) of the sol was established.

4. Conclusions

From the present investigation on the rheological behaviour of boehmite sols under closed condition the following conclusions can be drawn.

(I) Shear thinning behaviour, area of hysteresis in the flow curves and yield stress are the functions of particle–particle aggregation due to weak forces of attraction (e.g. van der Waals forces). A rapid development of particle–particle interconnectivities takes place during the ageing period from 15 to 36 days.

(II) Gel point or the point of sol–gel transition of boehmite sol is identified by the cross-over points of G'' and G'. The gel point of the sol appeared at the ageing time of 36 days. Before and after this point the sol tends to become viscous and elastic in character, respectively. A change in viscous to elastic character of the sols takes place with shifting the phase angle (δ) from about 90° towards 0°. At the ageing time of 36 days the phase angle (δ) becomes 45°; it indicates the purely viscoelastic character of the sol, i.e. the appearance of gel point. The formation of particle–particle interaction is slow at the initial stage (before 15 days) of ageing.

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