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# Effect of Surfactants on Bauxite Residues Suspensions Viscosity

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## **Abstract:**

Measurement of the rheological property of bauxite residue samples received from an Australian alumina refinery (red mud and neutralised mud suspension) has been carried out using a Brookfield viscometer. The plant samples were treated with two anionic surfactants (sodium polyphosphate and sodium laurate) in the laboratory and the effect of the surfactants on the residues viscosity was determined. It was found that the addition of sodium laurate, prepared with an excess of sodium hydroxide causes reduction of the viscosity of both red mud and neutralised mud while sodium polyphosphate shows very little effect on either samples. The suspensions exhibit non-Newtonian behaviour and obey the power law model over a range of solid concentrations at 75 °C.

**Author Keywords:** Red Mud, Bauxite residues, Rheology, Surfactant, Viscosity reduction.

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## 1. Introduction

The Bayer process is the most efficient method in the alumina refinery industry for the extraction of alumina from bauxite. This process generates residue known as **red mud** in large quantity. In a typical refinery, bauxite is dissolved in sodium hydroxide solution under pressure and elevated temperature to extract the alumina minerals leaving behind the iron, titanium and silica gangue minerals (red mud). The residue material is separated from the liquor (which contains dissolved alumina after the extraction process) in large settlers/clarifiers. After the residue is washed in counter-current decanters with hot condensate to recover the valuable caustic soda component, the mud is disposed. In some refineries, the residue is diluted with sea water in the plant before disposal, where part of the caustic soda component in the liquor is neutralised by salt ions such  $\text{Ca}^{++}$ ,  $\text{Mg}^+$ . This reduces the pH of the mud from 12-13 to 9-10. This process is commonly known in the industry as the seawater neutralisation process and its product is called **neutralised mud**. At the present, there is no viable process developed for utilising the bauxite residue, consequently this large quantity of waste material is required to be disposed economically and safely to the environment.

The common method for residue disposal is pumping the material to large settling ponds where on-land waste disposal is permissible [1, 2]. Typical problems associated with red mud pumping are high energy requirement, rapid wear of pipelines (due to erosion caused by the presence of large abrasive sand particles in some refineries), large land area required and significant environmental impact (due to the alkaline conditions of the liquor disposed with red mud). The magnitude of these problems can be reduced if the waste material is disposed at higher solid concentration. However this is at the expense of higher pumping cost since the apparent viscosity of the mud increases significantly as the solid concentration increases [3, 4, 5]. There is obviously incentive to reduce the residue viscosity at relatively high solid concentrations, so that the pumping cost can be minimised.

In general, the rheological behaviour of concentrated mud residues is affected strongly not only by solids loading, particle morphology and particle size distribution, but also by particle interactions. These interactions are influenced by chemical factors such as the presence of flocculant/deflocculant agents. The practice of adding flocculants during clarification and mud washing is already used widely in the industry to promote the settling of particles during the solids separation process. High molecular weight negatively charged anionic polyacrylates are commonly used for the flocculation of bauxite residue in clarifiers/settlers. For mud washing, a mixture of acrylate and non-ionic acrylamide is often used.

Most of the published literature on the rheology of flocculated residues is related to the behaviour of the material without surfactants [6-10] while very limited work exists on how this behaviour is affected by surfactants [12,16].

Residue suspensions, without surfactants, can be classified as non-settling homogenous slurries provided the large particles fraction in the solids is negligible. At concentrations below 10% by weight, it behaves like a Newtonian fluid with a constant viscosity which varies only with liquor concentration and temperature.

Between solid concentrations of 10% and 25%, mud suspensions exhibit the characteristics of shear thinning i.e. viscosity decreases with increasing rate of shear [2].

Capillary viscometry has been used to determine the relationship between shear stress and shear rate and the power law model is generally found suitable to describe the rheological behaviour of the suspension at low to medium solid concentrations [1, 11]. At higher concentrations, the suspensions become thixotropic and exhibit a yield stress in addition to the shear thinning behaviour [7]. The thixotropic behaviour means that the flow properties of the material are not only dependent on shear rate but also on time of shear and previous shear history. A vane-shear instrument was used [8] to measure the yield stress which defines the minimum shear stress that must be exceeded to start flow.

Hiroshue et al. [12] have conducted study of the effect of pH and surfactants on the dispersion of residue suspensions. They found that pH can influence the coagulation and dispersion of the suspension. Some extent of dispersion has been observed by the authors in the pH range of 8-11 at pH = 5. Complete dispersion the suspension, however can only be obtained using surfactant sodium hexametaphosphate (which is also known as sodium polyphosphate). The optimum concentration of the surfactant was found to be between 0.1 and 1% by weight.

Hashimoto et al. [16] have investigated the dispersion of mud residue in non-aqueous media and found that linseed oil is effective to disperse the material in hexane and cyclohexane solutions.

It is well established that the behaviour of bauxite residue is very much dependent on the types of bauxite (used in the digestion process) and flocculant (used in the separation process). Therefore, it is likely that the previous results are not applicable to mud residues from different refinery using different types of bauxite.

The present work is aimed to study the effect of surfactants on the rheology of red mud and neutralised mud samples received from an Australian refinery (Comalco Alumina Refinery in Gladstone, Queensland, Australia). Effective surfactants which are suitable to reduce the bauxite residue viscosity will be determined.

Other objective of this study is to provide process design information which may be used for the design of new equipment and/or the upgrade of existing equipment for the handling of the same material or similar.

Also the rheological data obtained from this work may be useful for researchers working in various programs currently conducted to explore the possible use of bauxite residues for agricultural, mining, industrial and waste treatment application [17].

In this work, sodium polyphosphate has been used since the phosphate group of surfactant is known for its ability to displace flocculant polymers such as polyacrylamide from clay particles [14] and the application of this surfactant as a dispersing agent for kaolinite has been demonstrated [13]. This surfactant was also used previously for the dispersion of bauxite residue [12].

Sodium laurate was chosen as it is a cheap biodegradable anionic surfactant which poses less environmental problems than those containing the phosphate group.

## 2. Materials and methods

Two mud samples were received from Comalco:

- (i) Red mud slurry from the last washer of the mud washing train (its solid concentration is approximately 540 g/L),
- (ii) Neutralised mud slurry from the plant neutralisation thickener underflow.

These suspensions were stored in screw top containers. The red mud pH was found to be approximately 12 while the neutralised mud was about 8.5.

The samples received were used directly and no attempt was made to alter the structure of the flocculated particles (e.g. stirring or adding more flocculant). For the preparation of suspensions at higher concentrations, the original mud was allowed to settle in containers and supernatant liquor was decanted. This supernatant liquor was kept for use in the preparation of samples of lower concentrations.

A Malvern size analyser (Mastersizer S model) was used to determine the sample particle size distribution. The results of the size distribution are shown in Table 1. The results are comparable to those for neutralised mud from QAL reported elsewhere [11].

Rheological measurements were carried out using a Brookfield rotational viscometer (Rheomat DVIII). All measurements of shear stress, shear rate and apparent viscosity were carried out in a temperature-controlled environment at 75°C to simulate typical plant conditions. The range of rotational speed was between 30 and 240 RPM corresponding to a shear rate range between 40 and 300 sec<sup>-1</sup>. No quantification of the extent of particles settling was established during the course of measurement. However for the given particle size distribution (refer to Table 1) it is expected that settling would be minimum since the large particle size fraction in the red mud samples is negligible.

Measurement of the samples rheology without surfactants was carried at solid concentrations in the range of 400 to 800 g/L at 75 °C.

Sodium polyphosphate (commercial name: hexametaphosphate, ratio P<sub>2</sub>O<sub>5</sub>/Na<sub>2</sub>O =0.9; average molecular weight =1733.39) supplied by Sigma was used to prepare surfactant solution in water.

Sodium laurate (0.2 M solution) was prepared by reacting lauric acid with caustic soda NaOH at the molar ratio NaOH : lauric acid of 1:1 and 10:1.

Both surfactants were added to residue suspensions at the dosage rates ranging from 0.5 to 5 % wt of surfactant/dry mud. All measurements with the use of surfactants were conducted with solid concentration of 500 and 800 g/L. After the addition of surfactant, measurements of shear stress at various shear rates were conducted using the Brookfield viscometer.

## 3. Results and discussion

### 3.1 Mud suspensions without surfactants

#### 3.1.1 Apparent viscosity

A typical plots of apparent viscosity (cP) versus shear rate ( $\text{sec}^{-1}$ ) for red mud (referred to as RM in the following text) is shown in Figure 1. A similar plot for neutralised mud (referred to as NM) is displayed in Figure 2. Both suspensions display a shear thinning behaviour as expected i.e. as the shear rate increases the apparent viscosity decreases. When the shear rate increases, the hydrodynamic forces exerted by the flow field become higher, consequently the flocculated red mud particles are presumably broken down into smaller particles and the liquid entrapped is gradually released. This results in decreasing viscosity.

The effect of increasing the suspended solid concentration on apparent viscosity is also shown in Figures 1 and 2. As the concentration is increased from 500 g/L to 800 g/L, for the shear rate of  $100 \text{ sec}^{-1}$  (which is a typical shear rate for pumping in pipeline) the apparent viscosity is approximately doubled from 20 cP to about 40 cP. Similarly, the viscosity of NM suspension was found to increase up to 70 % as its solid concentration increases from 500 g/L to 800 g/L.

For a given solid concentration and temperature, RM suspensions are apparently more viscous than NM. The ratio of the respective viscosities at a given shear rate is approximately doubled (refer to Figure 3). For the particular samples from this refinery, the observed reduction of viscosity may be due to the in-plant neutralisation process which may bring about changes to the flocculated particle structure (e.g. flocculants being washed away) and/or particle surface charges. These alterations may be responsible for some dispersion of the red mud particles resulting in a reduction of the apparent viscosity of the neutralised suspension.

A similar behaviour has been observed in the work of Hirose et al. [12] for RM residues washed in laboratory using water. These authors postulated that the reduction of viscosity may be due to the removal of flocculant during the laboratory washing process.

#### 3.1.2 Power law model

The measured shear stress and shear rate data for the residue samples were analysed according to the power law model (Ostwald-de Waele). The model equation is expressed in the following form:

$$\tau = K\gamma^n \quad (\text{Equation 1})$$

where  $\tau$  is shear stress (Pa)  
 $\gamma$  is shear rate ( $\text{sec}^{-1}$ )  
K is the power law constant (consistency index)  
n is constant (flow behaviour index)

A typical plot of  $\ln(\tau)$  versus  $\ln(\gamma)$  for RM suspension at 500 g/L solid concentration is shown in Figure 4. The linear relationship indicates that the power law model is satisfactory for the given concentration. In fact this behaviour was observed for all the samples used in this work in the range of solid concentrations

considered. The correlation factors  $R^2$  were found to be greater than 0.98. This indicates that the power law model is suitable to describe the rheological behaviour of both mud residues in the range of concentrations and the temperature considered in this study.

The values of K and n from all test measurements for suspensions at various solid concentrations are summarised in Table 2. The flow behaviour index n measured for all suspensions was found to be less than 1, thus in the range of concentrations considered they behave as pseudo plastic or shear thinning fluids.

### 3.1.3 Variation of indices K and n with solids concentration

As the solid concentration increases, it was observed that the consistency index K also increases and the following correlations were obtained for untreated red mud and neutralised mud respectively:

$$K = 0.0056 e^{0.0069 \times \text{solids concentration}} \quad \text{Correlation factor} = 0.91$$

$$K = 0.0042 e^{0.0059 \times \text{solids concentration}} \quad \text{Correlation factor} = 0.95$$

For the flow behaviour index n the following correlations are obtained:

$$\text{Red Mud: } n = -0.527 \times \ln(\text{concentration}) + 3.7755 \quad \text{Correlation factor} = 0.94$$

$$\text{Neutralised Mud } n = -0.3713 \ln(\text{concentration}) + 2.7791 \quad \text{Correlation factor} = 0.96$$

The fitting of K and n values to the above models are shown in Figures 5 and 6. As the correlation factor for these models above are relatively poor, their usefulness for design purposes may be limited.

## 3.2 Effect of surfactant on suspension viscosity

### 3.2.1 Sodium polyphosphate

The effect of sodium polyphosphate (PP) on the apparent viscosity of mud suspensions at 500 g/L solid concentration was determined for various surfactant dosage rates in the range between 0.5% and 5%. This is shown in Figures 7 and 8. It can be seen clearly that no appreciable reduction in viscosity was observed for either suspension.

At low surfactant dosage rate (e.g. 0.5%) there is no noticeable effect on viscosity. The reason behind this behaviour could be explained in terms of the charges of the flocculated particles (which are negative or neutral according to Fawell et al.[15]) and the negative charge of sodium polyphosphate, this causes the surfactant particles to remain in non-adsorbed conditions.

As the surfactant concentration is increased (e.g. 1%) it is observed that the viscosity also increases. It is possible that further addition of the surfactant leads to the excess of sodium polyphosphate in the solution which is not adsorbed on the suspended mud particles. Consequently destabilisation and flocculation occur, this causes the

viscosity to increase. This behaviour was also observed for the sodium polyphosphate/kaolinite system [13].

The effectiveness of sodium polyphosphate as dispersant agent for RM reported by Hirosue et al. [12] was not observed in this work. These authors reported that washed red mud samples display completely Newtonian behaviour and the mud apparent viscosity is reduced up to a factor of 5 after an addition of sodium polyphosphate of 0.2% wt. It is possible that the treatment of their samples in the laboratory (i.e. washing process using water) caused alteration to the flocculated particles structure (e.g. the removal of the flocculants) or the particle charge thus allowing sodium polyphosphate to be adsorbed more readily on the particles and the ensuing effectiveness of the dispersant was achieved.

### **3.2.2 Sodium laurate**

The effect of sodium laurate surfactant prepared at the NaOH : lauric acid molar ratio of 1:1 on the suspension viscosity was measured. No significant benefit in viscosity reduction was observed at this molar ratio. However at the molar ratio of 10:1 the benefit of the surfactant becomes more apparent. This is shown in Figures 9 and 10. For both types of suspensions, the surfactant was observed to be effective for the reduction of viscosity. The maximum benefit appears to occur at the surfactant dosage rates between 1% and 2%.

The benefit of sodium laurate at the high molar ratio could be explained partially using the flocculated hematite particle model postulated for red mud according to Fawell et al.[15]. The model is shown in Figure 11. In this model, it is postulated that in alkaline conditions (pH=13) the adsorption of anionic polymers such as polyacrylate polymer onto the negatively charged hematite particles can only take place in the presence of cations such as sodium. These cations cause neutralisation of the negatively charged particles thus allowing the anionic head group to be adsorbed onto the particles. In the case of the anionic sodium laurate, the availability of excess cation sodium in the surfactant solution may be responsible for the observed benefit of viscosity reduction.

Sodium laurate, when added to bauxite residue for the purpose of mud particle dispersion, is considered suitable for disposal with the residue to the environment as the surfactant is biodegradable over a short period of time. Therefore, the use of sodium laurate may not cause adverse impact to the environment. This aspect needs to be confirmed.

The use of sodium laurate, while beneficial in term of viscosity reduction, may lead to the alteration of the behaviour of the residue in storage ponds. It is possible that the mud yield stress and its angle of repose may be affected. Further investigation is required to determine the effect -if any- associated with the change in the stacking height of disposed residue due to the addition of sodium laurate surfactant on the management of land use.

#### **4. Conclusions**

The rheological investigation performed in this work shows that sodium laurate solution (prepared with excess in sodium ion) is an effective dispersing agent for red mud and neutralised mud suspensions while sodium polyphosphate was found to be unsuitable. The maximum effectiveness of the sodium laurate surfactant is reached when its dosage rate is between 1% and 2 % (dry weight surfactant/mud) It is suggested that, the excess of the sodium cation in the surfactant solution is responsible for its effectiveness as a viscosity reducing agent for bauxite residue suspensions.

#### **5. Acknowledgements**

The authors wish to thank Comalco for providing red mud and neutralised mud samples for measurements conducted in this work. Permission from the company to publish the data is also appreciated.

#### **Nomenclature**

$\tau$	shear stress (Pa)
$\gamma$	shear rate ( $\text{sec}^{-1}$ )
K	power law consistency index
n	flow behaviour index

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## Tables

Table 1: Particle size distribution of Comalco red mud and neutralised mud

Particle size distribution	Micron
D <sub>10</sub>	13
D <sub>50</sub>	2.9
D <sub>80</sub>	6.5

Table 2: Values of K and n for RM and NM suspensions

Concentration (g/L)	RM suspensions		NM suspensions	
	K	n	K	n
400	0.062	0.636	0.059	0.536
500	0.230	0.499	0.059	0.502
600	0.453	0.385	0.142	0.395
700	0.982	0.275	0.258	0.353
800	0.967	0.303	0.542	0.287

## Figures

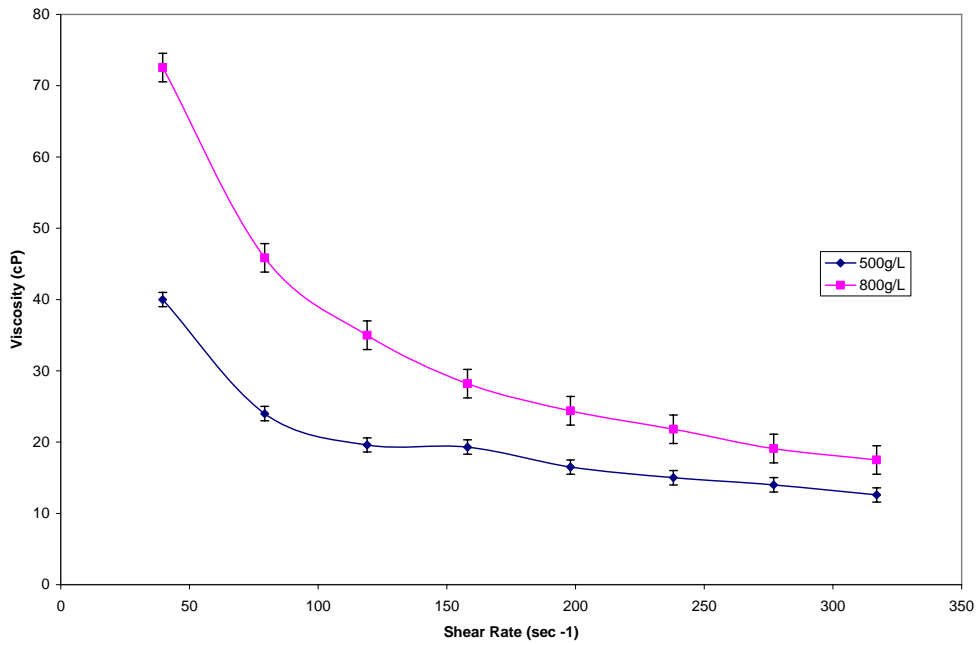


Figure 1: Apparent viscosity of RM suspensions

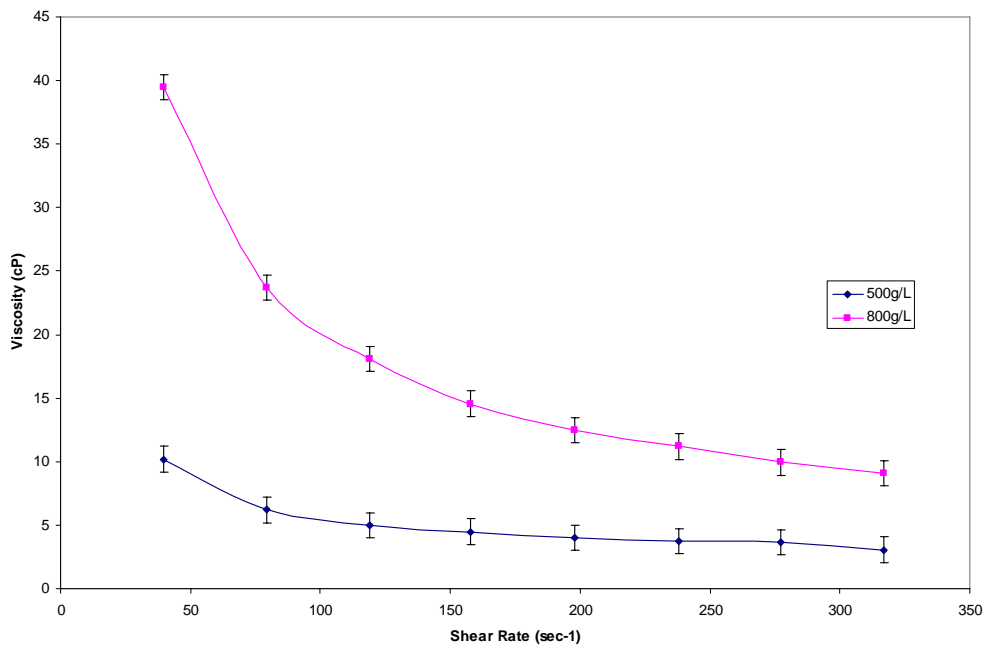


Figure 2: Apparent viscosity of NM suspensions

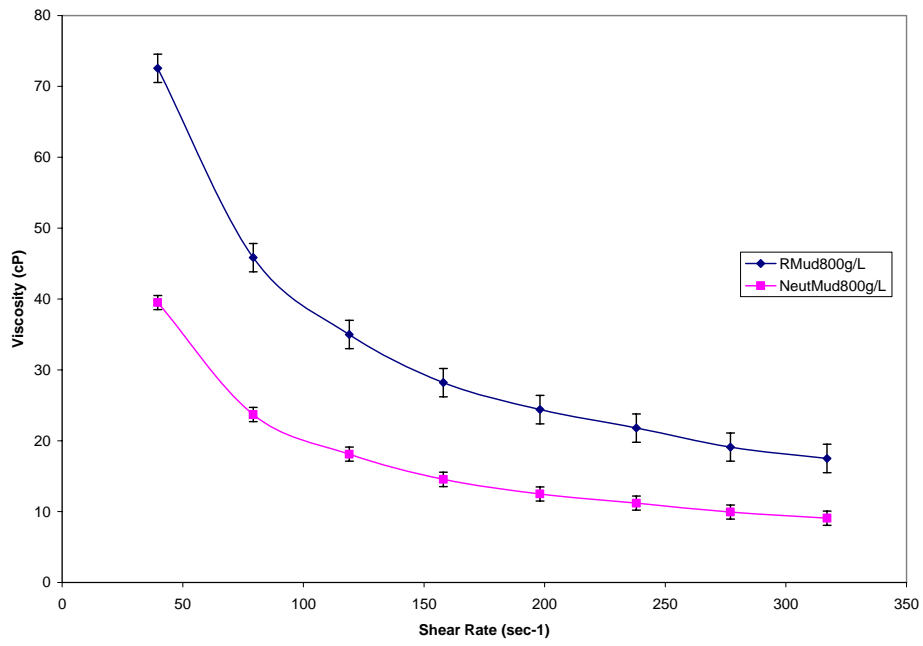


Figure 3: Viscosity of RM and NM at 800 g/L solids

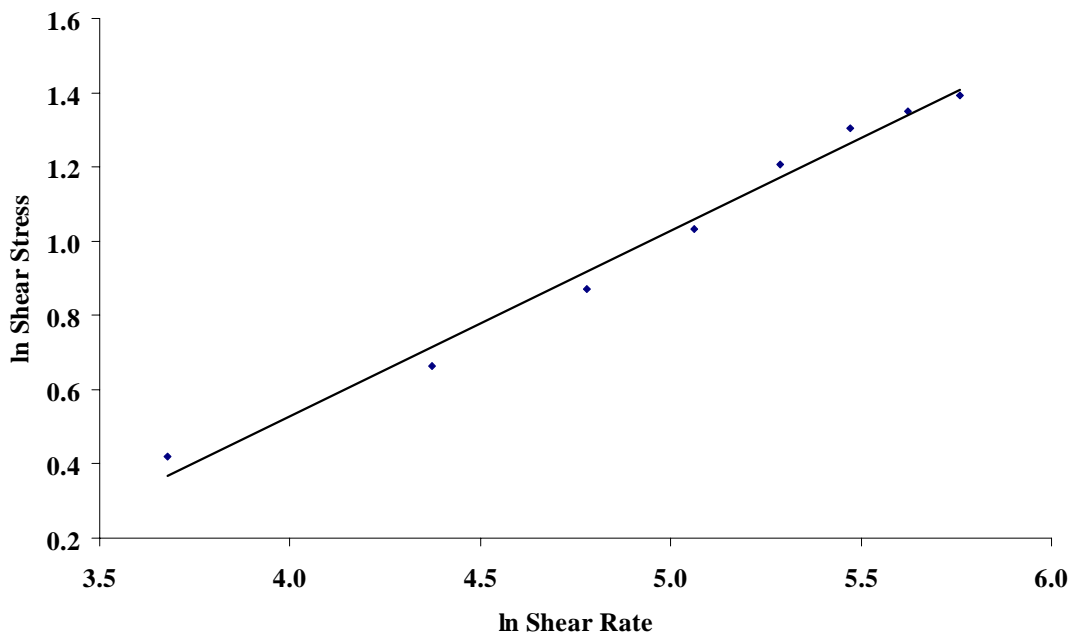


Figure 4: Power law model fitting, RM suspension at 500 g/L

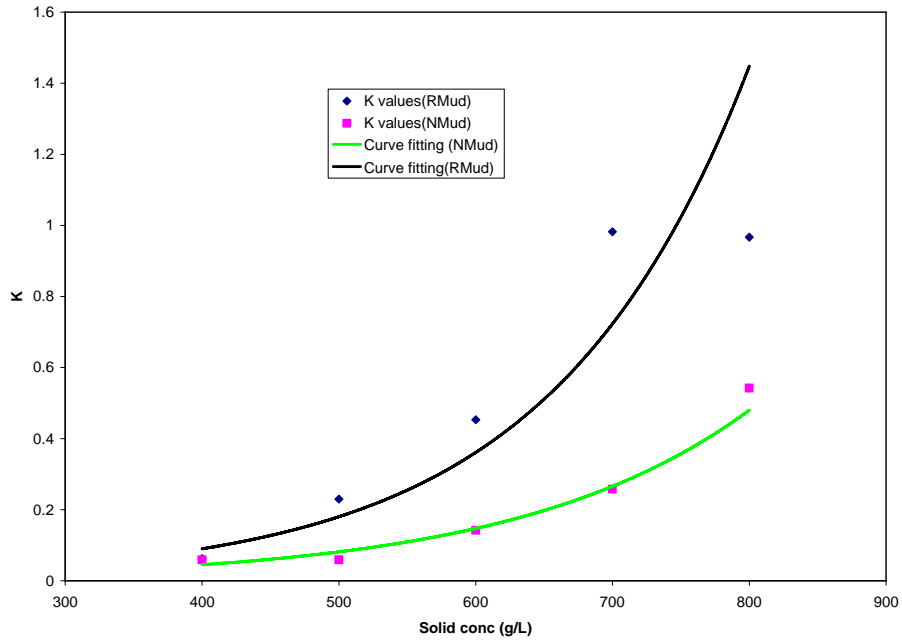


Figure 5: Correlation between K and solid concentrations

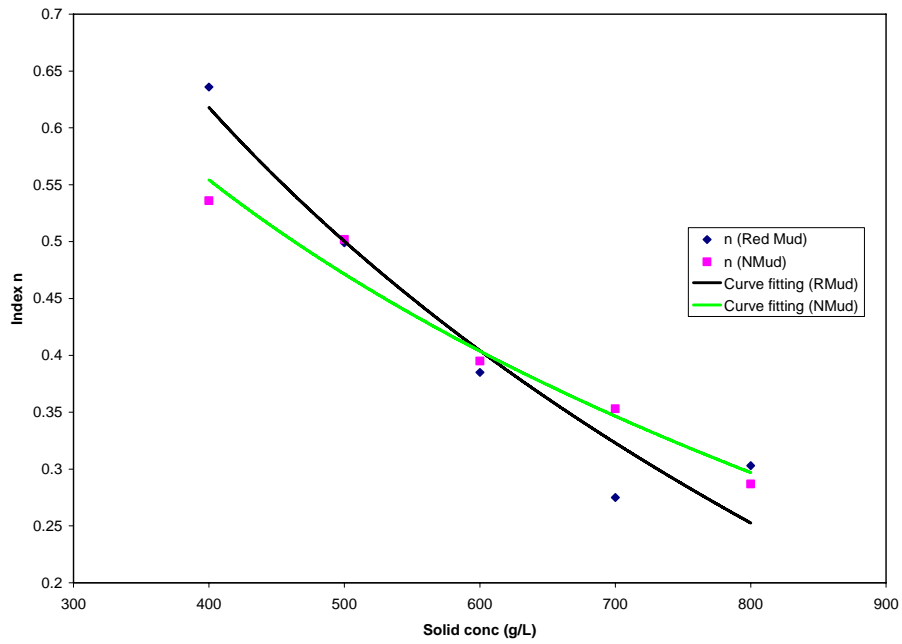


Figure 6: Correlation between n and solid concentrations

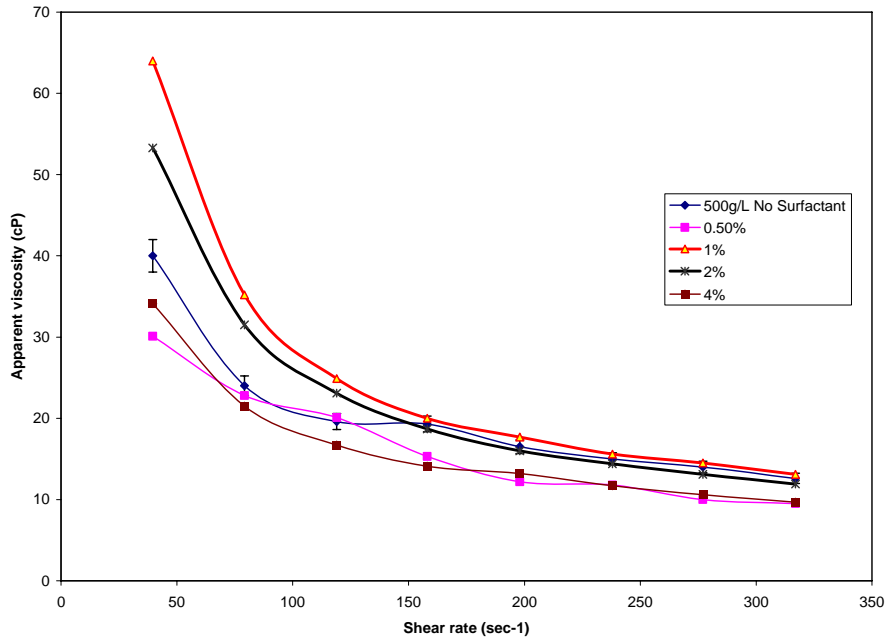


Figure 7: Viscosity of RM suspensions treated with PP surfactant

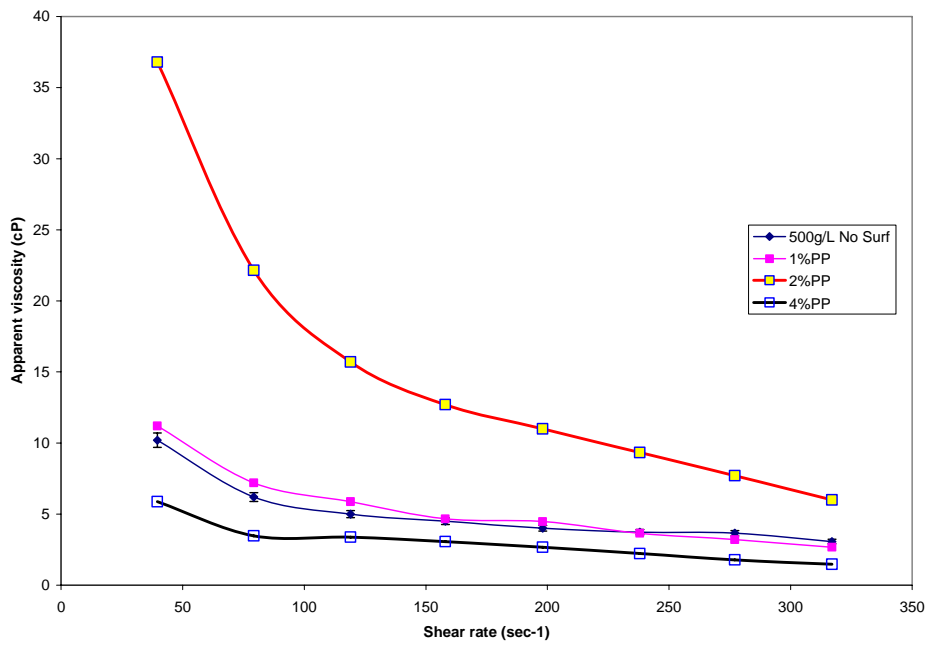


Figure 8: Viscosity of NM suspensions treated with PP surfactant

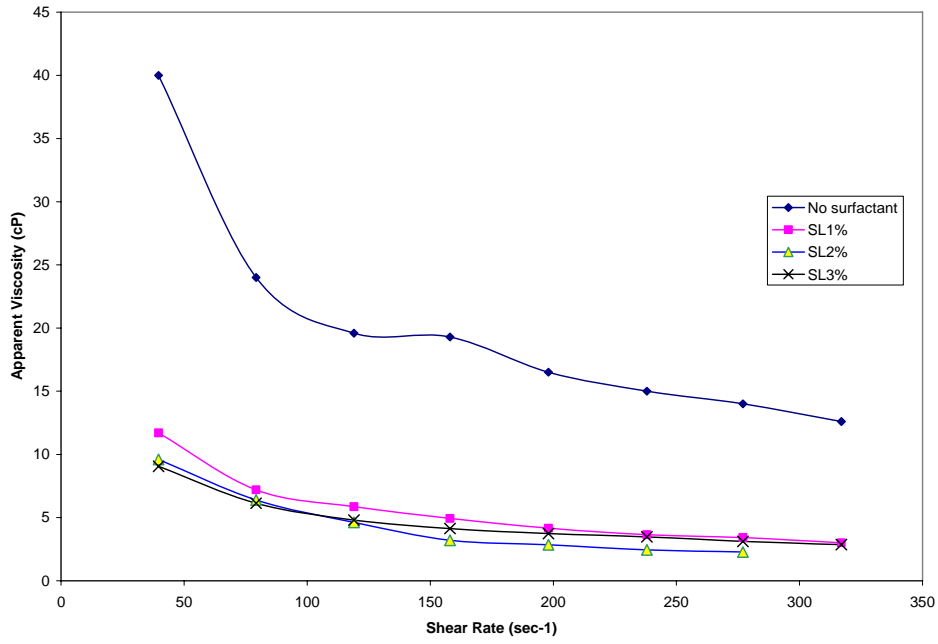


Figure 9: Effect of sodium laurate on RM suspension apparent viscosity

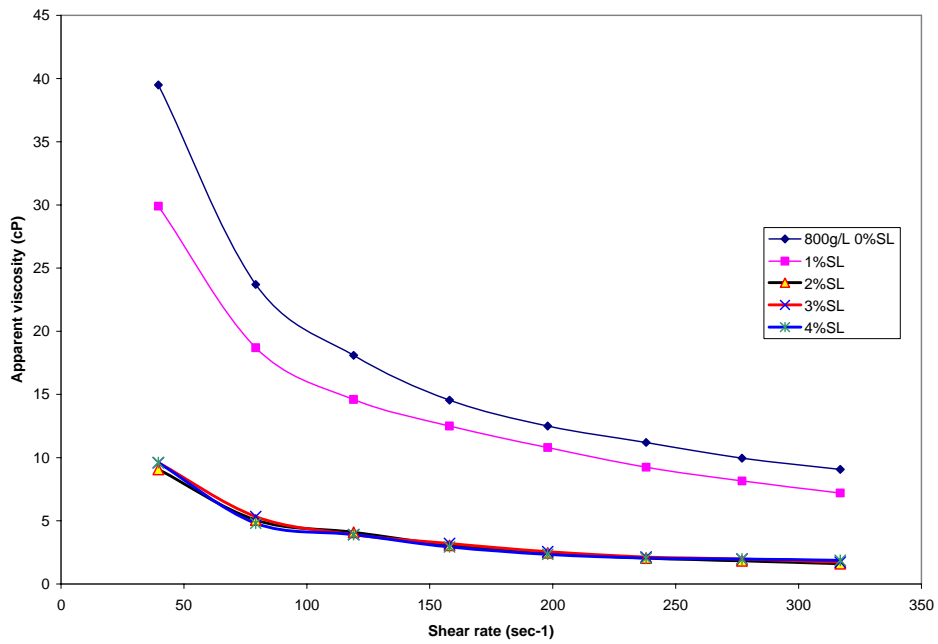


Figure 10: Effect of sodium laurate on NM suspension apparent viscosity

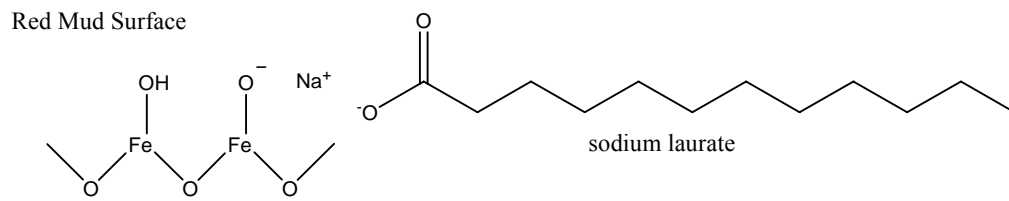


Figure 11: Proposed adsorption mechanism of Sodium Laurate onto RM surface