DEVELOPMENT OF SAPONIN EXTRACTED
FROM Sapindus laurifolia AS ADDITIVE

CHAPTER-4
DEVELOPMENT OF SAPONIN EXTRACTED FROM Sapindous laurifolia AS ADDITIVE

4.1: Introduction

The present work is an attempt to develop saponin, a natural surface active compound extracted from the fruit of Sapindous laurifolia plant as an additive to get relatively concentrated coal-water slurry. Sapindous laurifolia is one type of soap nut tree indigenous to both India and China and is available in abundance mostly in eastern zone of India. Saponin extracted from it is a complicated mixture of saccharine derivatives and belongs to a class of natural occurring non-ionic surfactants. The hydrophilic part of the molecule called glycon consists of saccharides such as glucose, galactose, rhamnose, xylose, pentose, etc. and hydrophobic part called aglycone consists of steroids and triterpene. The hydrophobic part is bonded through oxygen to the hemiketal or hemiacetal carbon of the saccharide residue which in turn is linked through oxygen linkages to other saccharide residues (Molecular structure 4.1).

Molecular structure 4.1: Saponin (White ball: Hydrogen, Blue ball: carbon, Red ball: Oxygen)

4.2: Experimental

4.2.1: Isolation of saponin from Sapindus laurifolia

The drupes of Sapindus laurifolia were collected from Paralakhemundi, the forest zone of southern Orissa, India. Pericarp of the drupes of Sapindus laurifolia were cut into pieces and were extracted four times with water at ambient temperature, and finally with hot water (90-95°C). The solid liquid ratio was maintained at 1:3 and the sample was soaked with water for 12 hours each time. The extract was concentrated on a climbing film through evaporation. On adding ammonium sulfate till saturation, solid mass started floating. The floated mass was separated and squeezed off to remove water. The floated
solid compound was extracted and recrystallized from n-butanol phase to give bushy thread-like mass which was identified to be saponin. A single spot was found in thin layer chromatogram of silica gel taking hexane:chloroform(1:3) as the eluant. The melting point was found to be 145°C as reported earlier[267].

4.2.2: Fluorescence measurement
Florescence spectral measurements were made on a Hitachi 650-40 Fluorimeter. Stock solution of the fluorescence probe, pyrene was prepared in pure methanol(AnalR grade, Sisco-chem). Various concentrations of saponin containing 1 x 10⁻⁶M of pyrene were prepared. The emission spectra of pyrene in between 370-480nm were recorded by exciting the saponin solutions at the absorption maximum (λmax) of pyrene in water (335nm).

4.2.3: Preparation of coal-water slurry
The coal-water slurry was prepared by agitating the coal-water mixture containing additives in a helical ribbon mixer at 50-150 rpm( to avoid particle disintegration) by using a variable frequency drive. The suspension has fair stability during the measurement for at least 48 hrs.

4.2.4: Rheological and zeta potential measurement
The rheological studies of the CWS were carried out using a HAAKE Rotational viscometer (Model RV 30), consisting of measuring drive unit, temperature vessel with circulator, sensor system and a data logger. A sensor system MV I was chosen for the rheological measurements. The sensor and the cup were cleaned and air-dried. About 100 ml of slurry was prepared at weight concentrations ranging from 55-64% by weight with distilled water. The additive concentration for coal-water slurry were varied from 0.4 - 1.2% by weight in steps of 0.2 % for different weight concentration of coal slurry. The variation in temperature was ± 0.1° C controlled through a constant temperature circulator bath connected to viscometer. All experiments were conducted at room temperature of 30° C. The pH of coal-water slurry with natural and commercial additives measured in a pH meter was in the range of 4.5-5.0.

The rheological measurement was controlled by a software rotation version 3.0. The best-fit model was fitted to the shear stress-shear rate data to obtain the nature of coal-water slurry. The various parameters such as shear stress, shear rate, true viscosity,
apparent viscosity and temperature along with the curve were displayed on the computer screen.

Zeta probe 24V(52-60 Hz) T3A equipped with microprocessor was used for the measurement of the zeta potential of coal particles containing 5% weight fraction of coal in water.

4.2.5: Static Stability tests
The coal-water slurry was prepared by agitating the coal-water mixture containing saponin in a helical ribbon mixer at 50-150 rpm (to avoid particle disintegration) by using a variable frequency drive at weight concentrations of 58%-65% and were then poured into glass cylinders of about 100ml. The top of the cylinders was sealed and the cylinders were stored at room temperature. The static stability of coal-water slurry was evaluated by applying rod penetration method[263,268] i.e. a glass rod of fixed weight and diameter was put into the slurry to observe whether soft sedimentation appeared during storage. The soft sedimentation was identified as it can be easily disintegrated by mild stirring and transferred to other containers without any difficulty. The appearance of soft sediment by days was used as an indicator of static stability.

4.3: Results and Discussion
4.3.1 Surface activity of the aqueous solution of saponin:

The surface activity of saponin has been determined by studying the fluorescence characteristics of saponin solution taking pyrene as fluorescent probe. Pyrene(Molecular structure 4.2) has a structured monomeric emission with five peaks out of which the first peak at 370 nm(I1) and third peak at 380 nm(I3) are sensitive to the polarity of the medium[267](Fig.4.1).

![Molecular structure 4.2: Pyrene](image-url)
Fig. 4.1: Monomer spectrum of pyrene

The intensity ratio increases with increase in the nonpolarity of the surrounding medium (Fig. 4.2) and hence the ratio $I_3/I_1$ is called as polarity parameter [269, 270].

Fig. 4.2: Changes $I_3/I_1$ of pyrene with change in polarity of the solvent.

Due to nonpolar nature of pyrene it prefers to partition to hydrophobic environment. The critical micellar concentration (CMC) of saponin has been determined through measurement of polarity parameter as a function of surfactant concentration. At very low concentration the emission spectrum of pyrene is similar to that in pure water with $I_3/I_1$ ratio = 0.63. With increase of saponin concentration the ratio gradually increases till a value of 1.5 is reached at around 0.8% of saponin (Fig. 4.3).
This value does not change with further increase of saponin. Appearance of a plateau in the polarity parameter versus [saponin] curve has been attributed to the consequence of micelle formation and the concentration at onset of plateau of this curve is considered to be CMC\(^{[271]}\). The gradual increase in the ratio has been attributed to the gradual decrease in the polarity of pyrene environment due to the formation of micelles in a step-wise manner. The micelles are evolved gradually through association of surfactant monomers to form premicellar aggregates such as dimers, trimers, tetramers\(^{[270,271]}\) etc. The step-wise association has been evidenced from the appearance of excimer, at low concentrations of saponin. The excimer is a complex formed between a ground state and excited state pyrene and it shows a broad peak at 480nm (Fig. 4.4).

**Fig. 4.4:** Monomer and excimer spectrum of pyrene in presence of saponin at 0.4% of saponin
Due to small size of the aggregates ground state and excited state pyrene molecules can be placed at suitable distance to form an excimer within the domain of the premicellar aggregates due to their small size. The intensity of the excimer increases due to the formation of more premicellar aggregates as the saponin concentration increases (Fig. 4.3). But once the micelles are formed in the solution, the intensity of the excimer goes down due to the distribution of pyrene in large domain of micelles. The formation of excimer decreases as the probability of the excited singlet P* to leave one micelle and interact with a ground-state pyrene from another micelle to form excimer during its excited lifetime is very low since the exit of pyrene from micelles is a millisecond phenomenon whereas fluorescence is a nanosecond phenomenon[273]. The excimers are formed at very low concentrations of saponin due to the large hydrophobic residue of saponin. The bulky hydrophilic head in the saponin molecule drive the step-wise growth of micelles[270,272](Scheme-4.1).

\[
\begin{align*}
M_1 + M_1 & \rightarrow M_2 \\
M_2 + M_1 & \rightarrow M_3 \\
& \vdots \\
M_1 + M_{k-1} & \rightarrow M_k, \quad n=2, 3, 4, 5, \ldots
\end{align*}
\]

Where \( M \) is the monomer of saponin

Scheme-4.1

4.3.2: Effect of coal loading

The apparent viscosity of coal-water slurry for coal-A, Coal-B and Coal-C is measured at shear rate 77 S\(^{-1}\) with 0.8 % weight(w/v) of saponin (around critical micellar concentration, CMC) by varying coal weight in the concentration range of 55-64%. The values are given in Table 4.1. The apparent viscosity is found to increase with solid weight concentration due to increase in particle-particle interaction.

Table 4.1: Effect of solid weight concentration on Apparent viscosity.

<table>
<thead>
<tr>
<th>Concentration Coal in CWS %</th>
<th>Apparent Viscosity, Pa.s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coal A (Low ash)</td>
</tr>
<tr>
<td>50.0</td>
<td>0.382</td>
</tr>
<tr>
<td>55.0</td>
<td>0.42</td>
</tr>
<tr>
<td>60.0</td>
<td>0.50</td>
</tr>
<tr>
<td>62.0</td>
<td>0.60</td>
</tr>
<tr>
<td>64.0</td>
<td>0.82</td>
</tr>
</tbody>
</table>
Beyond 64% weight fraction of coal the slurry becomes hard sediment and hence difficult to disperse. Variation of apparent viscosity with shear rate containing 64% and 60% of coal A, B and C and 0.8% of saponin are shown in the Figures 4.5-4.7. The similar behaviour of coal-water slurry has also been reported by other authors [44,274]. The apparent viscosity is found to increase with increase in ash content of the coal for the same weight concentration of coal-water slurry possibly due to strong interaction of the hydrophilic ash with water. Usually Increase in ash content leads to strong aggregation of coal and formation of gel state resulting in increase of the viscosity of the slurry[44].

Fig.4.5: Rheological behaviour of coal A sample with variation of shear rate having loading 60% and 64% containing 0.8% of saponin.

Fig.4.6: Rheological behaviour of coal B sample with variation of shear rate having loading 60% and 64% containing 0.8% of saponin.
4.3.3: Effect of additive concentration

The apparent viscosity of coal-water slurry (64%) is found to decrease with increase in additive concentration till a constant value is obtained beyond 0.8% weight of saponin as shown in Figure 4.8. Viscosity is a property of liquid which resists the motion of different layers present in it. This opposing force arises largely due to van der Waal’s forces of the molecules present in the different layers. Saponin adsorption at coal-water
interface increases the surface hydrophobicity as well as hinders the close approach of the different layers due to steric barriers offered by the head groups of saponin. This leads to the decrease in interaction among particles present in the layers. The steady decrease of viscosity of the slurry occurs as long as saponin continues to adsorb on coal particles. But once the critical micellar concentration is achieved in the solution, the saponin monomers prefer to aggregate to form micelles. This limits its monomer activity[275] and hence no further adsorption of saponin takes place onto coal-water interface. It is reported that surfactant adsorbed as monomer at the interface[275-278] and hence the effect of saponin on apparent viscosity is labeled up beyond its CMC i.e 0.8%(w/v).

4.3.4: Rheological behaviour studies of Coal-Water slurry

Figures 4.9-4.11 show the plots of shear stress with variation of shear rate of coal-water slurry(64% weight fraction) in presence of 0.8% of saponin and a commercially available surfactant, sodium dodecyl sulphate(SDS).

![Fig.4.9: Rheological behaviour of coal A sample in presence of saponin and SDS](image-url)
In all cases a linear shear-stress, shear-rate relationship with an initial shear-stress threshold is found. Thus these fluids belong to Bingham plastics fluids obeying equation 4.1.

$$\tau = \tau_0 + \eta \gamma \quad \ldots (4.1)$$

Where $\tau$ and $\gamma$ denote shear stress and applied shear rate respectively. $\tau_0$ is the yield stress and $\eta$ is defined as co-efficient of rigidity. The yield stress and apparent viscosity values measured at shear rate of 77 S$^{-1}$ in the wt. concentration range of 55-64% for all coal samples are given in Table-4.2. On analyzing the rheological measurement data of
coal water slurry it is found that coal samples A, B and C have non-Newtonian characteristics in the weight concentration range 55-64%.

Table 4.2: Apparent viscosity, Yield stress for Coal-A, Coal-B & Coal C at Shear rate of 77 S\(^{-1}\) for different CWS wt. concentrations

<table>
<thead>
<tr>
<th>Wt. Concentration, C(_{\text{w},}) %</th>
<th>Apparent Viscosity (PaS)</th>
<th>Yield Stress (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coal A</td>
<td>Coal B</td>
</tr>
<tr>
<td>55</td>
<td>0.42</td>
<td>0.46</td>
</tr>
<tr>
<td>60</td>
<td>0.50</td>
<td>0.54</td>
</tr>
<tr>
<td>62</td>
<td>0.60</td>
<td>0.72</td>
</tr>
<tr>
<td>64</td>
<td>0.82</td>
<td>0.97</td>
</tr>
</tbody>
</table>

4.3.5: Effect of pH on zeta potential of coal and apparent viscosity of coal-water slurry

The electrophoretic mobility (zeta potential) of the coal particles (5% in water) have been measured with variation of pH and are shown in Figures 4.12-4.14. The bare coals exhibit an isoelectric point at around 5.4-6.5, which falls within the same range as reported earlier[57,85]. However, in the presence of saponin the zeta potential is decreased in all cases with concomitant shift of isoelectric point of all coals towards alkaline pH(Table 4.3)

![Graph](image)

Fig. 4.12: Variation of zeta potential of Coal A with change in pH in presence and absence of saponin.
Fig. 4.13: Variation of zeta potential of Coal B with change in pH in presence and absence of saponin

Fig. 4.14: Variation of zeta potential of Coal C with change in pH in presence and absence of saponin
Table 4.3: Isoelectric point (IEP) of different Coals in absence and presence of saponin and SDS.

<table>
<thead>
<tr>
<th>System</th>
<th>Isoelectric point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naked Coal A</td>
<td>5.4</td>
</tr>
<tr>
<td>Coal A with additive</td>
<td>6.8</td>
</tr>
<tr>
<td>Coal A with SDS</td>
<td>6.5</td>
</tr>
<tr>
<td>Naked Coal B</td>
<td>6.1</td>
</tr>
<tr>
<td>Coal B with additive</td>
<td>6.5</td>
</tr>
<tr>
<td>Coal B with SDS</td>
<td>6.1</td>
</tr>
<tr>
<td>Naked Coal C</td>
<td>6.5</td>
</tr>
<tr>
<td>Coal C with additive</td>
<td>6.8</td>
</tr>
<tr>
<td>Coal C with SDS</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Coal surface contains polar groups such as –COOH and –OH attached to the hydrocarbon skeleton connected by cross links[3,52]. Depending on the pH of the solution the polar groups get protonated or ionized when suspended in water (scheme 4.2).

\[
\text{RCOOH}_2 \xrightarrow{\text{H}^+} \text{RCOO}^{-} + \text{H}_2\text{O}
\]

Scheme-4.2

At acidic pH protonated hydroxyl and carboxyl group will render positive charge and at alkaline pH dissociated hydroxyl and carboxyl group would render negative charge to coal surface. These charges account for its zeta potential when electric field is applied. The decrease in zeta potential may be attributed to the mechanical displacement of the shear plane being projected some distances beyond the original shear plane or coverage of a fraction of coal surface due to the adsorption of bulky surfactant molecules at coal-water interface. Such decrease in zeta potential due to the adsorption of surfactant at the silica-water interface has been reported[279]. The shift of isoelectric point is due to large number of –OH and –COOH groups present in adsorbed saponin which may also be dissociated and protonated depending on the pH of the solution. The apparent viscosity of all coal-water slurry (60% w/v) are found to decrease with increase of pH as shown in Figures 4.15-4.17.
Fig. 4.15: Effect of pH with viscosity for coal A (Coal concentration= 60%, Shear rate= 77 1/s and saponin 0.8%)

Fig. 4.16: Effect of pH with viscosity for coal B (Coal concentration= 60%, Shear rate= 77 1/s and saponin 0.8%)
1.2

The electrostatic repulsion between intense negative charges developed on coal surface due to the ionization of the polar groups prevents particle-particle association as the pH of slurry increases. This results in reduction of apparent viscosity. The yield stress is computed graphically from the plot of shear stress versus shear rate at a particular pH. The plot of yield stress with variation of pH (Figure 4.18), shows a slow increase in yield stress up to certain pH beyond which there is a sharp and steady increase.

Fig. 4.17: Effect of pH with viscosity for coal C (Coal concentration= 60%, Shear rate= 77 1/S and saponin 0.8% )

Fig. 4.18: Plot of yield stress versus pH of the slurry containing 60% weight fraction of coal and 0.8% of saponin
decrease in yield stress. The maximum yield stress is obtained at a pH that nearly coincides with the isoelectric point (around 6-7 pH). Since at isoelectric point the residual charge on coal particle becomes zero, greater cooperative interaction of the saponin-adsorbed coal particles occurs resulting in highest yield stress. Hence they settle down relatively easily. To make the slurry flow at this pH one has to pump the slurry more to make it flow than any other pH. The slow increase of yield stress before isoelectric point is probably not affecting the apparent viscosity of the slurry too much and hence a continuous decrease in apparent viscosity is observed with increase in pH in all cases.

Saponin is by nature nonionic, but because of the presence of large number of group containing oxygen having lone pairs of electron sometime behave like anionic nature. This may be the reason for which the effect of SDS and saponin are more or less equal. In fact during measurements of pK of a number of aldimines in presence of nonionic and ionic surfactant assemblies Misra et al[280] have seen that nonionic surfactant assemblies behave in a similar way to anionic surfactant assemblies. Mishra et al[10,86] have also observed the similarity in behaviour between Brij-35, a nonionic surfactant with an anionic surfactant NaDBS during their studies on the adsorption characteristics at coal-water interface.

4.3.6: Effect of temperature on apparent viscosity of coal-water slurry.

The apparent viscosity of coal-water slurry is found to decrease exponentially with increase of temperature as shown in Figures 4.19 and 4.20. This is attributed to decrease in inter-particle attraction due to increase in kinetic energy of the coal particles. The relation between viscosity and temperature may be represented by a simple Arrhenius expression[122] as presented in equation-4.2 which on rearrangement yields equation-4.3.

\[ \eta = A \exp\left(\frac{E}{RT}\right) \quad (4.2) \]

\[ \ln (\eta) = \frac{E}{RT} + \ln (A) \quad (4.3) \]

where \( \eta \) is the viscosity at a particular shear rate, \( E \) is the fluid –flow activation energy, \( T \) is the temperature in Kelvin, \( A \) is fitting parameter and \( R \) is Universal gas constant. A linear plot with correlation coefficient near about 0.99 (Figure 4.21) is obtained for coal-water slurry containing 64% of coal. The fluid flow activation energy is found to depend on the type of coal used being highest for coal A and lowest for coal C.
Fig. 4.19: Effect of temperature on apparent viscosity for coal A, B, and C (Coal concentration= 60%, Shear rate= 77 1/S and saponin 0.8%)

Fig. 4.20: Effect of temperature on apparent viscosity for coal A, B, and C (Coal concentration= 64%, Shear rate= 77 1/S and saponin 0.8%)
Fig. 4.21: Arrhenius plot of viscosity versus temperature for coal A, B, and C (Coal concentration= 64%, Shear rate= 77 1/S and saponin 0.8%)

4.3.7: Stability of the slurry

Table 4.4 shows the static stability of the coal-water slurry using the additives. The slurry is found to be pretty stable. The Coal A is however, found to be more stable due to less amount of ash content in the sample.

Table 4.4: Static stability
Stability of CWS with days at different weight concentrations (1%)

<table>
<thead>
<tr>
<th>Wt. Concentration</th>
<th>No. of Days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coal-A</td>
</tr>
<tr>
<td>58</td>
<td>18</td>
</tr>
<tr>
<td>60</td>
<td>21</td>
</tr>
<tr>
<td>62</td>
<td>23</td>
</tr>
<tr>
<td>64</td>
<td>30</td>
</tr>
</tbody>
</table>

4.3.8: Mechanism of stabilization of coal-water slurry.

For a hydrophobic solid like coal the most probable mechanism of adsorption of saponin at coal-water interface is the adsorption of surfactant with its hydrophobic group being anchored on the coal surface while the hydrophilic chain has to remain dangled in the bulk water. This orientation of saponin at the coal-water interface is further supported by adsorbing hederagenin, the hydrolyzed product of saponin (which is essentially nonpolar) on coal surface. Hederagenin[267] was synthesized by hydrolyzing 10 grams of Saponin with 100 ml of aqueous methanol(1:1) containing 5% hydrochloric acid.
resulting sticky mass was separated and washed with petroleum ether to remove the oils present in it. The insoluble substance on crystallization from methanol gives rhombic crystals of hederagenin (m.pt. 328-329°C). The rheological behaviour of coal-water slurry treated with 0.8% of hederagenin was studied, the viscosity found to remain unchanged. The decrease in viscosity in the presence of saponin therefore, excludes the possibility of orientation of hydrophobic towards bulk aqueous phase. The hydrocarbon part of the molecule lies flat on the hydrophobic surface and hydrophilic part protrudes to bulk water molecules (Figure 4.22). The bulky glycosides heads are hydrated and form an effective barrier around each particle. The mechanical barrier increases the resistance of the dispersed particles to maintain a mechanical shock and prevent them for coalescence when they collide inhibiting the close approach of one particle to another (Figure 4.23). The stabilization of the coal-water slurry by the additive is mostly due to steric reasons as the zeta potential of coal is decreased with adsorption of the additive.

Fig.4.22: Schematic representation of a coal particle with adsorbed saponin, the terpenoid part sitting on its surface and the glycoside part being oriented toward bulk water phase
Saponin, a surface active compound extracted from the fruits of plant sapindous laurifolia has been developed as a cost effective and environment friendly additive for stabilization of coal-water slurry. Since these surfactants contain carbon, hydrogen and oxygen only, in the combustion of coal-water slurry, the contribution of the surfactants to the amount and fusion temperature of ash produced is negligible. The results confirm the use of saponin as a suitable additive for coal-water slurry similar to commercially available additive such as sodium dodecyl sulphate. Production of a concentrated coal-water slurry from a non-coking coal with 64% coal in present of saponin with stability of approximately one month against 58-60% percent of coal with 3-4 hrs stability without the additive indicates the efficiency of saponin as a good stabilizing agent for concentrated coal-water slurry.