

# Dynamic surface tension of coal–water slurry fuels

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Experiments were conducted to measure the dynamic surface tension of coal–water slurry (CWS) mixtures containing various types of surfactants and with different coal loadings. A maximum air bubble pressure technique measured the dynamic surface tension. The coal used for the CWS had 55  $\mu\text{m}$  volume mean diameter (VMD) and was mined from the Upper Elkhorn seam, Virginia. Five surfactants were selected for the study: one non-ionic alkylphenol ethoxylate (NP-100), and four anionic surfactants; branched dodecylbenzene sulfonic acid (DDBS-hard), linear dodecylbenzene sulfonic acid (DDBS-soft), a sodium salt of a branched alkylbenzene sulfonic acid (1223H), and a sodium salt of sulfonated fatty acid (1840X). To determine the critical micelle concentration (CMC), the static surface tension was also measured using a du Nouy ring tensiometer. Measured values of dynamic surface tension are presented for 40 and 50% CWS mixtures, with surfactant concentrations ranging from 0.1 to 5.0% in weight.

**(Keywords: slurries; surface tension; measurement)**

Coal–water slurry (CWS) fuels are attractive as an alternative to fuel oil due to their lower cost and similarity to oil with respect to convenience in transporting and handling. CWS fuel needs to be finely atomized to be combusted satisfactorily. Atomization characteristics of slurry fuels, like any other liquid fuels, significantly affect the combustion performance. The basic physics of atomization of slurries is not well developed. There is a weak theoretical base for characterizing droplet sizes with defined properties<sup>1</sup>. However, an intrinsic difficulty in studying CWS fuels is their diversity in chemical and physical content, which largely depends on the geographic location where the coal was mined. A universal correlation will be quite difficult to expect for CWS atomization, and an individual study of coal from a particular seam is essential.

Viscosity and surface tension are two significant properties in determining atomization characteristics of most liquid fuels. The viscosity of CWS is a function of shear rate and is orders-of-magnitude larger than water. Such high values of the CWS viscosity makes the atomization considerably difficult. It is generally agreed that CWS exhibits a weak shear-thinning behaviour at low and intermediate shear rates, and becomes Newtonian at higher shear rates where atomization occurs. The effect of dynamic surface tension on CWS atomization has not been evidenced to date. In fact, the effect of static surface tension has not been studied well either. There is little consensus concerning the effect of 'static' surface tension on droplet size of CWS sprays<sup>2</sup>. This lack of agreement, it is believed, may be due in part to the assumption that static surface tension can represent the surface characteristics of slurries even under the high

shear rates of atomization. It is the contention of the present work that the dynamic surface tension, rather than the static surface tension, is the more appropriate parameter of CWS atomization.

The addition of various dispersants, wetting agents and rheology enhancers is essential in obtaining the higher coal loadings that produce the higher energy densities for continuous combustion and high heating values. Under the quasi-equilibrium conditions of low shear rates, the static surface tension of the fluid is an appropriate measure of the fluid's ability to form small radius droplets. The static surface tension may be obtained through a du Nouy ring technique. However, the surfactants presented in the CWS formulation do not reach an equilibrium concentration throughout the solid–liquid or liquid–vapour interfaces at higher shear rates. Dynamic surface tension should be a more appropriate measure in accessing the atomization characteristics at high shear rates.

The dynamic surface tension of a fluid is simply a measurement of the surface tension at a particular rate of surface formation or shear rate. The static and dynamic surface tension values are the same for pure fluids, such as water. The values of dynamic surface tension for slurry mixtures containing various additives may be much higher than the corresponding static surface tension because insufficient time exists for the migration of surfactant additives to the atomized interface from the bulk mixture. The difference between the two surface tension values enlarges at higher shear rates, and allows less time for the surfactant migration.

The dynamic surface tension here is measured by the maximum bubble pressure technique<sup>3</sup>. Results of

dynamic and static surface tension of CWS mixtures at several coal loadings and with five different surfactants, each at five concentrations spanning their critical micelle concentration (CMC), are presented in this paper.

EXPERIMENTAL

CWS fuel

The CWS fuel was produced from coal mined from the Upper Elkhorn seam, Virginia. The coal was ground at the US Department of Energy, Pittsburgh Energy Technology Center, to a volumetric mean diameter (VMD) of 55 μm, with the size distribution spanned to 200 μm. The size distribution of the coal powder was measured by a Leeds and Northrop Microtrac standard range analyser. Proximate and ultimate analyses of the coal under test are included in Table 1. Note that this coal, with high carbon and reasonably low ash content, is typical of that used in boiler combustion applications. All CWS mixtures contained a basic

Table 1 Proximate and ultimate analyses of dry powdered bituminous coal from the Upper Elkhorn seam, Virginia<sup>a</sup>

Proximate analysis (wt%)	
Volatile matter	36.75
Fixed carbon	60.69
Ash	2.56
Heating value (high), kJ kg <sup>-1</sup>	34 741
Ultimate analysis (wt%)	
C	83.66
H	6.38
N	1.56
S	0.77
O	7.63

<sup>a</sup>Data from the US DOE-Pittsburgh Energy Technology Center, Pennsylvania

additive of 0.5% Pfizer Flocon 4800C Xanthan biopolymer stabilizer, which was necessary to keep the coal powder suspended in water. A preliminary experiment showed that the Flocon 4800C did not influence the surface tension of CWS mixtures.

Dynamic surface tension measurement technique

Figure 1 illustrates the operating principle of the maximum bubble pressure tensiometer technique. A capillary is inserted vertically to a depth of 10 mm into the vessel holding the sample under test. The capillary is formed from Teflon that is not wetted by CWS and has an outer radius of 0.49 mm, which is small enough to nullify the effect of hydrostatic deformation of the bubble as it emerges from the orifice<sup>3,4</sup>. As bubbles are formed, grow and detach from the tube orifice, the bubble pressure varies due to changes in bubble radius. The maximum pressure is reached as the bubble radius is at a minimum at the outer orifice radius. The dynamic surface tension is calculated from measurements of the maximum bubble pressure and evaluating the relation over a range of bubble frequencies<sup>5</sup>:

$$\sigma = (p_{max} - \rho gh)r_c/2 \tag{1}$$

Here  $\sigma$  is the surface tension,  $p_{max}$  is the maximum bubble pressure,  $\rho$  is the fluid (CWS) density,  $g$  is the gravitational constant,  $h$  is the height of the fluid above the orifice, and  $r_c$  is the capillary outer radius. The Kruss Model BP-10 tensiometer was adopted for the dynamic surface tension measurements and proved to be effective over a range of 2–10 bubbles s<sup>-1</sup> for coal loadings formulated up to 50%. The bubble formation frequency is directly related to the surface expansion rate:

$$\gamma = Q/\pi r_i^3 \tag{2}$$

where  $\gamma$  is the surface expansion rate in s<sup>-1</sup>,  $Q$  represents the volume flow rate of the injected gas (nitrogen),  $r_i$  denotes the orifice inner radius. Thus, the surface expansion rate is a proportional measurement of the rate of shear strain. The expansion rate has values that are roughly three orders-of-magnitude higher than the bubble frequency, as detached bubble radii are larger approximately by an order-of-magnitude compared to that of the orifice radius<sup>6</sup>.

The accuracy of the tensiometer was tested by measuring the surface tension for distilled and deionized water. The result ensured a satisfactory accuracy showing less than a ±1% deviation from the surface tension values listed in Reference 7.

Tested surfactants

A rotary tumbler mixed dry coal powder with deionized and distilled water and the Flocon 4800C stabilizer to yield the base CWS to which the surfactants were later added. Five surfactants were selected for the study: one non-ionic alkylphenol ethoxylate (NP-100), and four anionic surfactants; branched dodecylbenzene sulfonic acid (DDBS-hard), linear dodecylbenzene sulfonic acid (DDBS-soft), a sodium salt of a branched alkylbenzene sulfonic acid (1223H), and a sodium salt of sulfonated fatty acid (1840X). Each of the five different surfactants was added at five different weight concentrations to give a total of 25 CWS samples at a single coal loading. The selected surfactants are widely used in the pigment and

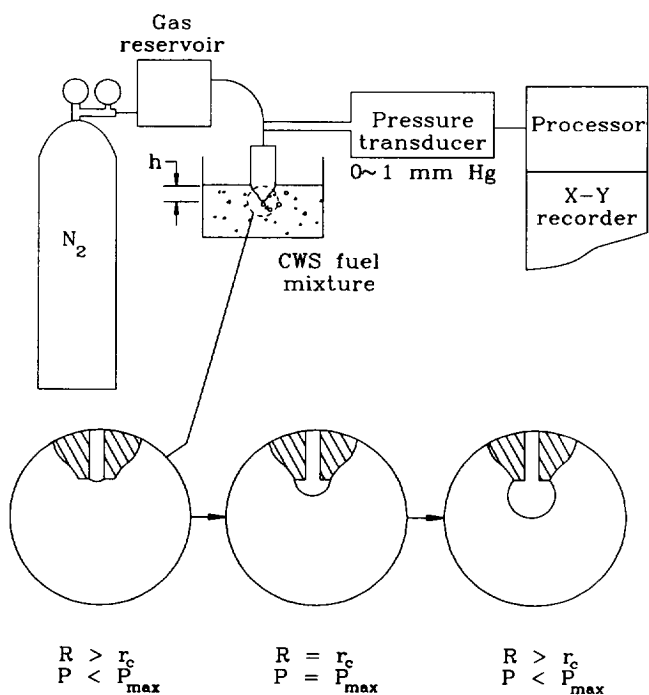


Figure 1 A schematic illustration of the maximum bubble pressure technique

paint industries<sup>8</sup>, and their formulae are presented in Table 2. (For simplicity, the surfactants will be identified by their brand names in the present paper.)

The static surface tension is minimized at a certain concentration of surfactant, which is called a critical micelle concentration (CMC). Surfactant concentrations greater than the CMC do not further decrease the static surface tension. The CMC can be determined from static surface tension measurements using a du Nouy ring tensiometer. A typical measurement of aqueous solution of NP-100 shows a CMC of 0.0041%, where the extended line from the steeply decreasing data meets the nearly constant regime (Figure 2).

Table 2 also presents a summary of the CMC of all surfactants in an aqueous solution, and in 40 and 50% CWS mixtures. A significant increase of CMC is observed when coal powder is added, and which is primarily due to the absorption of surfactant at the porous surfaces of the coal particles. The absorption isotherm for surfactants in CWS may be implied through the change in CMC with coal concentration. The static surface tension of the solid-liquid slurry formulation is almost entirely dependent on the surface tension of the liquid phase<sup>9</sup>. The CMC showed an increase with increasing coal concentration and as the total coal-water interface area was increased.

## RESULTS AND DISCUSSION

Since the CMC mostly ranged above 0.1% weight concentration for all surfactants, the dynamic surface tension measurement for CWS was performed at or above this 0.1% concentration. Figure 3 shows the results for 50% CWS mixture with NP-100 surfactant. The other four surfactants demonstrated qualitatively similar behaviour. The static surface tension of CWS mixtures approached that of pure water ( $72 \text{ mN m}^{-1}$  at temperature,  $T=25^\circ\text{C}$ ) when the surfactant concentration was decreased to zero, and approached that of the aqueous solution when the surfactant concentration was higher than the CMC. For the ranges of surfactant concentrations in-between, CWS exhibited higher static surface tension values than the aqueous solution at the same surfactant concentration. Consequently, the CWS also had higher CMC concentrations than their aqueous counterparts. This is likely due to the absorption of surfactants by coal particles that reduce the active concentration of surfactant in the bulk of the CWS mixture.

When the surfactant concentrations exceeded the CMC of 0.1%, the static surface tension of the CWS mixture

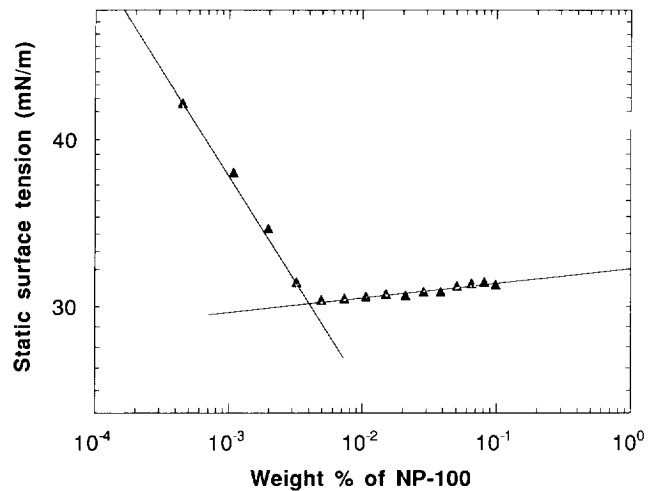


Figure 2 Static surface tension versus NP-100 weight concentration in aqueous solution showing critical micelle concentration (CMC) of 0.0041%

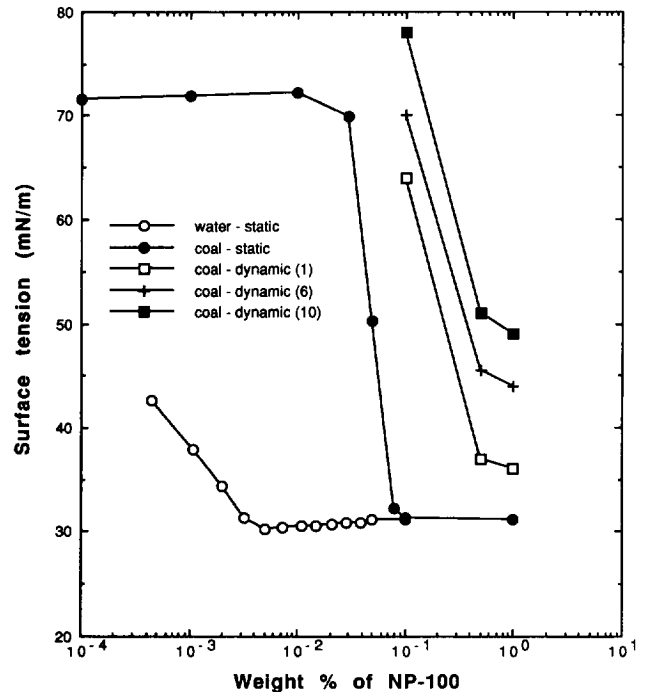


Figure 3 Static and dynamic surface tension of 50% weight CWS mixture with NP-100 (numbers in parentheses represent the bubble frequency  $\text{s}^{-1}$ )

Table 2 Critical micelle concentration (CMC) of aqueous and coal-water slurry (CWS) mixtures with five different surfactants

Surfactant		Critical micelle concentration (wt%)		
Brand name	Content	Aqueous solution	40% CWS	50% CWS
NP-100	Alkylphenol ethoxylate	0.0041	0.075	0.10
DDBS-hard	Branched dodecylbenzene sulfonic acid	0.1100	0.310	0.36
DDBS-soft	Linear dodecylbenzene sulfonic acid	0.0830	0.150	0.30
1223H	Sodium salt of branched alkylbenzene sulfonic acid	0.1200	0.250	0.50
1840X	Sodium salt of sulfonated fatty acid	0.0500	0.350	0.35

remained constant and equivalent to the surface tension of the counterpart aqueous solution. This suggests that the static surface tension of slurry mixtures is essentially equivalent to its counterpart in aqueous solution when enough time is given for the surfactant to migrate. For the case of non-absorbing silicon oxide particles suspended in liquid, a previous study<sup>9</sup> showed that the static surface tension remained nearly constant to the surface tension of the equivalent solution without the particles for a wide range of solid weight loadings. The present finding showed a consistency in that once the CMC was reached for CWS mixture, the coal particles were saturated, i.e. they were no longer absorbent and the static surface tension approached that of the equivalent aqueous solution, as for the slurry containing non-absorbent particles.

The dispersing mechanism of surfactant in the dynamic cases will be quite different. Surfactants in aqueous solutions are dispersed by molecular diffusion alone. However, the surfactant dispersion rate in CWS mixtures (beyond the CMC) will be significantly reduced due to the physical blocking of coal particles. The dynamic surface tension at different bubble frequencies (Figure 3) showed noticeably higher values than its static surface tension counterpart. The dynamic surface tension also showed a dramatic increase with increasing bubble frequency, since the volume expansion rate was faster with higher bubble frequency and less surfactant could migrate to the bubble surface. The static surface tension can be considered equivalent to the dynamic surface tension measured at zero bubble frequency.

Dynamic surface tension measured with different surfactants at the maximum bubble frequency of  $10\text{ s}^{-1}$  for 50% weight CWS mixtures is presented in Figure 4 and tabulated in Table 3. For a pure CWS mixture without surfactant (but with 0.5% Flocon added), the dynamic surface tension ranged from 80.5 to 84.0  $\text{mN m}^{-1}$ . These values of dynamic surface tension with no surfactant were higher than that of water,  $72\text{ mN m}^{-1}$  at the same temperature ( $T=25^\circ\text{C}$ ). This higher dynamic surface tension is believed to be due to the large increase of the total interface due to the presence of coal, and in part to the higher viscosity of the CWS mixture. Although not shown, the dynamic surface tension of CWS without surfactant exhibited a gradual increase with increasing bubble frequency from 1 to  $10\text{ s}^{-1}$ , which was not observed for any single-phase fluid, such as water. These observations lead to a conjecture that the dynamic surface tension of slurries is dependent upon not only the type and concentration of surfactant, but also upon the loading level of solid particles.

The dynamic surface tension at  $10\text{ bubbles s}^{-1}$ , Figure 4, showed persistent decreases up to about 1% surfactant concentrations, which were several times higher than the CMC of the same 50% CWS mixtures. This further decrease in the dynamic surface tension beyond the CMC is believed to be primarily a result of the presence of coal in the slurries, that restrains the migration of the surfactant. Gradual decreases were observed thereafter, indicating that a nearly saturated surfactant concentration had been reached. The surfactant concentration of approximately 1%, separating the steep decrease from the saturated regions, could be considered as a 'dynamic' CMC. The surfactant concentration should be maintained at a level at or higher than that of this dynamic CMC to appreciate fully the benefit of the surfactant effects. The CWS mixture with 5% weight concentration of NP-100 was so viscous that bubble pressure measurement was not possible. High concentration polymers from the non-ionic NP-100 did

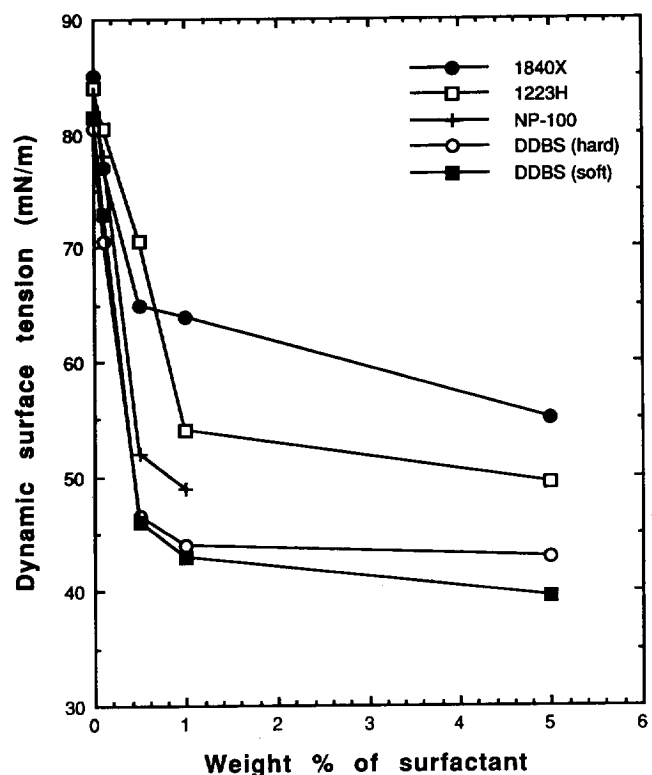


Figure 4 Dynamic surface tension of 50% weight CWS mixture with different surfactant concentrations under bubble frequency of  $10\text{ s}^{-1}$

Table 3 Dynamic surface tension ( $\text{mN m}^{-1}$ ) of 40 and 50% weight CWS mixtures containing five different surfactant concentrations measured at  $10\text{ bubbles s}^{-1}$

Surfactant concentration, wt%	40% weight CWS					50% weight CWS				
	0.0	0.1	0.5	1.0	5.0	0.0	0.1	0.5	1.0	5.0
NP-100	75.5	67.0	41.2	39.5	39.0	83.5	78.0	52.0	49.0	-
DDBS-hard	74.0	66.5	41.2	39.8	37.2	80.5	70.5	46.5	44.0	43.0
DDBS-soft	74.0	72.3	40.3	38.6	37.7	81.5	73.0	46.0	43.0	39.5
1223H	74.5	71.5	48.0	48.7	40.0	84.0	80.5	70.5	54.0	49.5
1840X	71.5	70.3	64.2	59.2	49.3	85.0	77.0	65.0	64.0	55.0

not allow distinctive growth and detachment of air bubbles, and the pressure measurement was significantly biased.

For the case of 40% loading CWS mixtures, dynamic surface tension results at 10 bubbles  $s^{-1}$  showed qualitatively similar trends in terms of the effectiveness of surfactants (Figure 5). When a higher ranking was provided for the surfactant, reducing the dynamic surface tension the greatest, DDBS-soft ranked the highest and 1840X scored the lowest rank for both 40 and 50% CWS mixtures. At a fixed surfactant concentration, the dynamic surface tension of 40% CWS was lower than its counterpart of 50% CWS. The saturated level of dynamic surface tension also showed lower values for 40% CWS, which supports the previous discussion of the increasing restraining effect of suspended coal particles upon surfactant migration with increasing coal surface areas.

These effects are more clearly shown by selectively presenting the dynamic surface tension data for the best (DDBS-soft) and the least effective (1840X) surfactants for the 40 and 50% CWS mixture (Figure 6). The dynamic surface tension for 40% CWS mixture showed lower values than the 50% CWS data, and the trend was consistent with the other three surfactants with intermediate effectiveness. The dynamic surface tension varied by up to 50% for different types of surfactants. These variations in dynamic surface tension may contribute to the alteration of the CWS atomization characteristics.

All the presented data were repeatable within uncertainties of  $\pm 2\%$ . A  $\pm 2\%$  scatter is considered to be fairly acceptable for the variable nature of the experiment, such as the inhomogeneity of coal particle sizes and shapes.

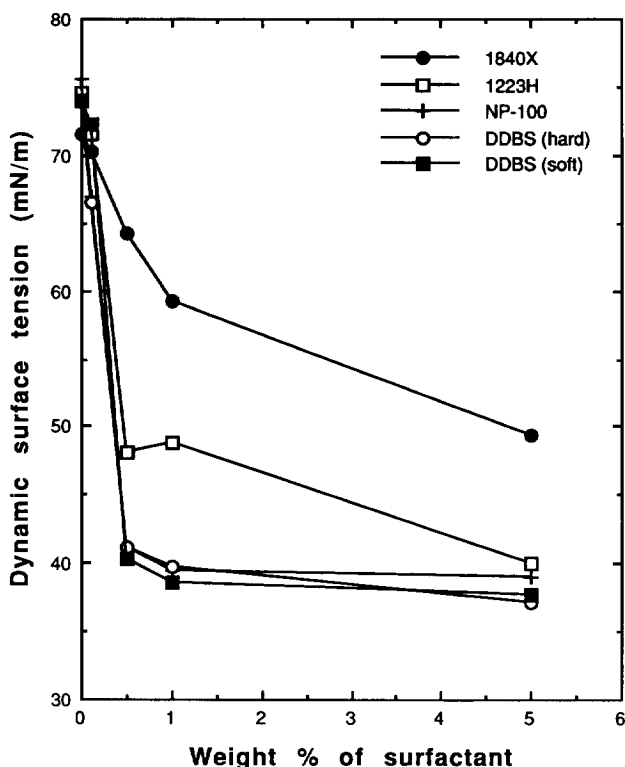


Figure 5 Dynamic surface tension of 40% weight CWS mixture with different surfactant concentrations under bubble frequency of 10  $s^{-1}$

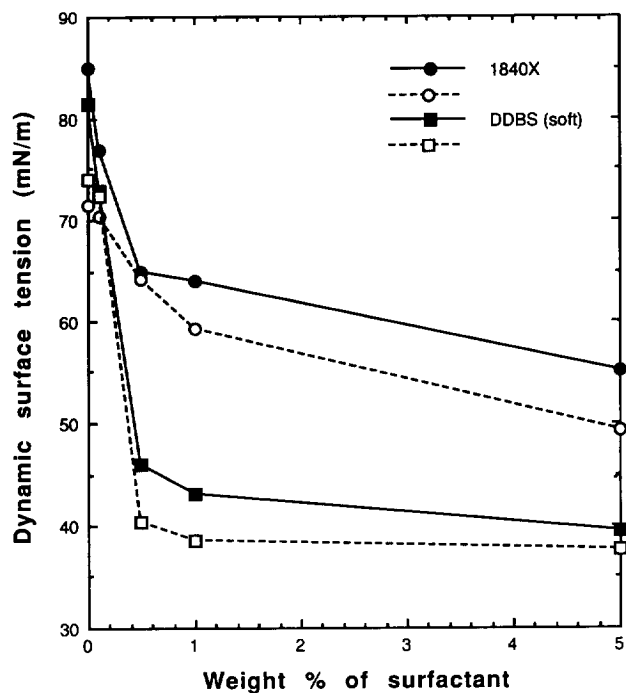


Figure 6 Dynamic surface tension measured at 10 bubbles  $s^{-1}$  for 1840X and DDBS-soft: —, 50% CWS; ---, 40% CWS

## CONCLUSIONS

This experimental study characterized the interfacial characteristics of CWS mixtures by measuring both the static and dynamic surface tensions. Experiments were performed with both 40 and 50% weight CWS containing five different surfactants at five different weight concentrations. The fundamental conclusions reached are:

1. The maximum air bubble pressure technique has been successfully applied to measuring the dynamic surface tension of CWS mixtures.
2. The critical micelle concentration (CMC) of CWS mixtures is considerably higher than for an aqueous solution, due to the absorption of surfactant by coal particles. When the CMC was met, the static surface tension values of CWS mixtures were identical to those of the corresponding aqueous solutions.
3. The values of dynamic surface tension for all mixtures are significantly higher than their static surface tension values, and increases with increasing bubble frequency.
4. For the tested surfactants, the dynamic surface tension continuously decreases beyond the CMC, up to approximately 1% surfactant concentration. The absorption of surfactant by coal is maximized at the CMC, and the further decrease in dynamic surface tension is primarily due to decrease in physical blocking of the suspended coal particles against the surfactant migration.
5. The values of dynamic surface tension of CWS mixtures showed wide variations for different surfactants, while their static surface tensions were almost identical to each other.
6. The dynamic surface tension of the CWS mixtures showed an increase with increasing coal weight concentration. It is believed that this is primarily because of the increase in interfacial surfaces and the

increase in the absorption of surfactant with increasing coal concentration.

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