



# Adsorption of PEO/PPO triblock co-polymers and wetting of coal

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## Abstract

The adsorption characteristics of PEO/PPO/PEO triblock co-polymers on coal were investigated using surface tension and contact angle measurements. Although these surfactants have been widely used as wetting agents, it was observed that they increased the hydrophobicity of coal at concentrations below about  $10^{-6}$  M. Surface tension studies were carried out to explain the reasons for this behavior. The surface tension versus concentration profiles displayed three distinct regions. In region I, surface tension decreased linearly and monomers were proposed to be the dominant species. This region extended to a surfactant concentration of about  $10^{-6}$  M. In region II, a transition region between regions I and III, dimers, trimers, etc., were considered to form. In region III, micelles formed and surface tension was independent of concentration. The concentration at which monomers associate to form dimers, etc., is referred to as the critical association concentration (cac). The contact angle of coal increased when concentration was raised from low values to the cac. It decreased when the reagent concentration was above the cac. Finally, at concentrations above the cmc, the wetting of coal was complete and contact angle was zero. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* PEO; PPO; Coal

## 1. Introduction

Block co-polymers of ethylene and propylene oxide find use in many industrial applications, such as pharmaceutical, biomedical, agricultural, environmental, cosmetic and textile industries. In these applications, they are utilized as wetting agents, emulsifiers, stabilizers etc. [1]. The am-

phiphatic properties of such reagents arise from the presence of PPO and PEO blocks. It is well-known that polypropylene oxide (PPO) is hydrophobic and insoluble in water, whereas polyethylene oxide (PEO) is hydrophilic and soluble in water. The adsorption and micelle formation involving triblock co-polymers appears to be more complex than conventional low molecular weight surfactants. There is a considerable amount of discrepancy in the literature with regard to the formation of micelles and the cmc of

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Table 1  
Cmc and  $N_{agg}$  for Pluronic L-64 determined by different techniques at various temperatures

Method	Temperature (°C)	cmc (M)	$N_{agg}$	Reference
Light scattering	27	$2.4 \times 10^{-3}$	–	
	34.5	$9.7 \times 10^{-4}$	–	[11]
	40	$3.1 \times 10^{-4}$	–	
	40		19	[12]
	60		85	
	28	$6.9 \times 10^{-3}$	–	
	30	$3.4 \times 10^{-3}$	–	[13]
	33	$1.7 \times 10^{-3}$	–	
Sedimentation velocity	40		54	[10]
	42		88	
Differential dye adsorption	25	$6.8 \times 10^{-6}$	–	[9]
Surface tension	20	$1.7 \times 10^{-4}$	–	[7]
	25	$6.9 \times 10^{-5}$	–	[8]
	25	$4.2 \times 10^{-6}$	–	[9]
	25	$7.0 \times 10^{-6}$	–	[1]

this class of surfactant. Earlier studies, in which light scattering and ultra-centrifugation techniques were used, indicate that triblock co-polymers do not form micelles [2–5]. Other studies suggested micelle formation in the form of a PPO core surrounded by a hydrated PEO shell [1,6–13]. Studies with Pluronic surfactants, a commercial series of triblock co-polymers, show large differences in cmc and aggregation number ( $N_{agg}$ ). The available data for Pluronic L-64 are given in Table 1. It appears that the results depend on the measurement techniques. The cmc varied by three orders of magnitude from one method to another. The light scattering method usually gave larger values ( $0.97 \times 10^{-3}$  to  $6.9 \times 10^{-3}$  M) compared with the surface tension method ( $4.2 \times 10^{-6}$  to  $1.7 \times 10^{-4}$  M).

Very limited information is available in the literature on adsorption of block co-polymers on surfaces of solids. Kayes and Rawlings [14] studied adsorption of PEO/PPO triblock co-polymers on polystyrene latex and found that the Langmuir model could be used. They suggested that polymer molecules attached to the latex through PPO segments, while the hydrophilic PEO groups extended into the solution as tails. The thickness of the adsorbed layer depended on the molar mass of the PEO groups and bulk polymer concentration.

Several investigators have proposed that the adsorbed PPO blocks formed small loops or were tightly coiled on the surface [14–16]. The area covered by each molecule was determined to be 2.85, 3.20, 5.90, 6.51, 15.10, 17.52 and 24.26 nm<sup>2</sup> for Pluronics L-61, L-62, L-64, F-38, F-68, F-88 and F-108, respectively [14]. The adsorbed amount was around 1.00 mg m<sup>-2</sup> for these surfactants. In the case of silica, both the PEO and PPO chains adsorbed, giving thin layers of constant thickness. The thickness of adsorbed layer was comparable with the thickness of PEO layers on silica [16]. The adsorbed amount was very low (0.35–0.40 mg m<sup>-2</sup>) and independent of the PPO content in the range between 0 and 30% PPO. In comparison, the adsorbed amount was 0.20 mg m<sup>-2</sup> in the case of a reagent with a 4000 molecular weight and 50% PPO content. The adsorbed layers were also found to be thin in the case of all the polymers (about 2–5 nm) by Tilberg et al. [17] and Malmsten et al. [18]. The thickness of the layer was also found to increase with particle size [19]. The area occupied by a block co-polymer molecule at a hydrophobic surface was found to be greater than those observed at the air–water interface [20,21] and considerably less than those at a hydrophilic surface, e.g. silica–water interface [22].

Table 2  
Selected properties of the PEO–PPO–PEO triblock co-polymers used in this study

Pluronics	Number of PO groups	Number of EO groups	$M_w$	HLB <sup>a</sup>
L-44	23	20	2200	12
L-62	30	17	2500	7
L-63	30	21	2650	11
L-64	30	26	2900	14
P-65	30	38	3400	17
P-103	56	39	4950	9
P-104	56	60	5900	13
P-105	56	74	6500	15

<sup>a</sup> HLB value is a measure of the hydrophilic/hydrophobic ratio of a given surfactant and frequently used to determine the emulsification power of surfactants.

The wetting power of a surfactant containing ethylene oxide groups usually increases with the concentration of surfactant and the number of ethylene oxide groups [7,23]. However, Chander et al. [24] observed that ethoxylated octyl phenols, which are normally used as wetting agents at high concentrations, increased the hydrophobicity of coal at lower concentrations. Increasing the hydrophobicity of coal selectively is important in the flotation process where the ash and sulfur are aimed to be rejected from the coal structure to produce a cleaner burning fuel. Building on the findings with ethoxylated octyl phenols, triblock co-polymers were good candidates for imparting selective hydrophobicity on the coal surface owing to their wider variety and more flexible structures. Hence, the wetting characteristics of coal in the presence of various triblock co-polymers were investigated using a modified contact angle measurement technique. Surface tension studies were also carried out to estimate the structures of the adsorbing molecules in water as a function of concentration. The effects of variables such as the reagent concentration and molecular weight were studied in both types of tests and the results are discussed in the following sections.

## 2. Methods and materials

Surface tension measurements were performed with a Kruss Digital Tensiometer K10T [25] using the Wilhelmy Plate method. Water used in this

study was obtained from a Barnstead 210 Biopure Distilled Water System, which was equipped with a Q baffle system to produce pyrogen-free water with a resistivity of at least 1.5 Mohm. This water was used in the experiments without any pH adjustment since its pH was observed to be constant between 5.6 and 5.8 in all the experiments. The glassware used was cleaned with a chromic acid solution. The acid was then thoroughly removed from the glassware using double-distilled water. All surface tension studies were carried out at a constant temperature of 21°C.

The captive bubble technique was employed to measure the contact angles for the coal–air–water system as a function of surfactant concentration. The classic captive bubble technique was modified so as to produce readings that would represent the heterogeneous structure of coal surface. To achieve this, about 50 measurements were made at pre-selected locations on a given substrate such that approximately 10 readings  $\text{cm}^{-2}$  were obtained. A normal distribution curve was observed to fit the distributions of contact angles. Hence, the surface could be characterized by two independent parameters, the mean and the standard deviation of the contact angle distribution. The coal used was a piece from the Pittsburgh coal seam. It was polished carefully to avoid contamination using standard polishing techniques.

The surfactants used in this study were obtained from BASF Corporation, Washington, NJ (Table 2 and Fig. 1; [26]). They were water soluble

and were used as aqueous solutions in the concentration range from  $10^{-9}$  to  $5 \times 10^{-1}$  M.

### 3. Results and discussion

#### 3.1. Surface tension studies

##### 3.1.1. Surface tension as a function of time

During initial phases of the study, it was observed that surface tension measurements were affected by the time elapsed after placing the solution in the cell and the actual measurement. Therefore, tests were carried out as a function of time and surfactant concentration using a fixed volume of solution (50 ml) in a cylindrical glass cell 4.5 cm in diameter. The solutions were gently stirred after being placed in the cell to enhance diffusion of surfactant molecules without causing any surface turbulence. Surface tension measurements were taken at pre-set time intervals for a period of about 1 h. The measurements were repeated four times to ensure reproducibility. The averages of these readings and the corresponding 95% confidence intervals are presented in Fig. 2. At the lowest concentrations tested,  $10^{-9}$  M,  $10^{-8}$  M and  $2 \times 10^{-8}$  M, surface tension did not change with time, probably because of insufficient amounts of reagent. These concentrations were not considered in further evaluation of the results. At concentrations greater than  $3 \times 10^{-8}$  M, the surface tension decreased with time and eventually reached a constant value, as can be seen in Fig. 2. The results may be explained by a mechanism involving slow diffusion of surfactant molecules. For the purpose of this discussion, the surface tension at long times were taken as the

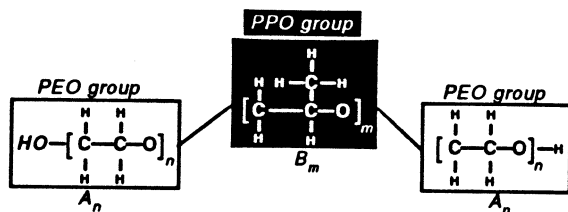


Fig. 1. Structural formulae of block co-polymers used in this study:  $n$ , number of EO groups;  $m$ , number of PO groups.

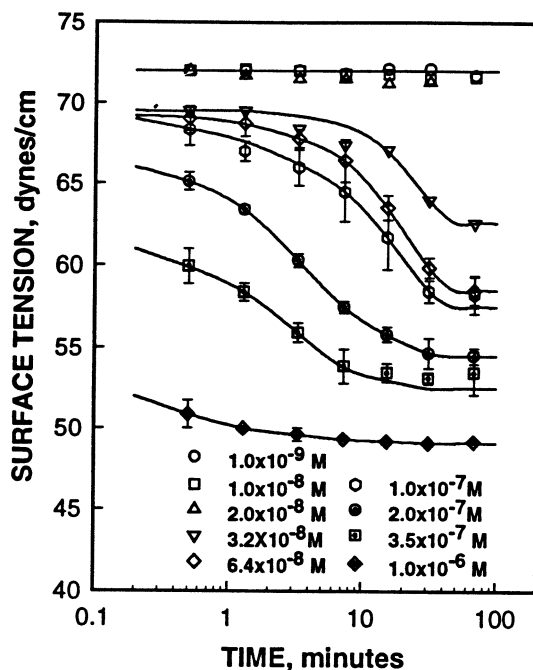


Fig. 2. The effect of conditioning time elapsed between the placement of the solution in the measurement cell and the measurement of surface tension for Pluronic L-64.

equilibrium values. The time needed to reach equilibrium decreased with increasing concentration, implying a diffusion-controlled process. The time-dependent phenomena might involve adsorption of slowly diffusing but more surface active species. To determine diffusion effects, the results of surface tension measurements are given in Fig. 3 with and without stirring. The results show that conditioning time is important in the concentration range from  $3 \times 10^{-8}$  to  $10^{-6}$  M. The difference between the data of Alexandridis et al. and that obtained in this study, presented in Fig. 4, may be attributed to variations in time of conditioning. This figure also confirms that time effects are important mainly at concentrations below  $10^{-6}$  M. Therefore, all solutions were gently stirred prior to surface tension measurements.

##### 3.1.2. Effect of surfactant concentration and molecular weight

Recent surface tension data reported in the literature for various aqueous PEO/PPO triblock

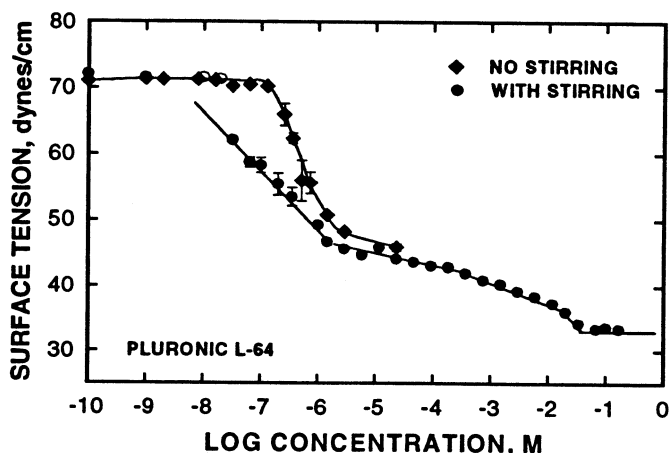


Fig. 3. The surface tension of Pluronic L-64 surfactant as a function of concentration for the gently stirred and non-stirred solutions.

co-polymer solutions show unusual characteristics [20,27,28]. A change was observed in the slope of the surface tension versus concentration curves at a characteristic concentration, after which the surface tension values continued to decrease until a constant value was reached. The second break in the curve is attributed to the formation of micelles and there is a general agreement. However, conflicting suggestions were made by various investigators to explain the first break. For example, Hecht and Hoffmann [28] suggested that the first break in the curve was due to the broad molecular weight distribution of the compounds. The highly surface active component begins to aggregate in the solution at this point, whereas the less surface

active material does not. It is only the second break in the curve where all the reagent forms micelles. Alexandridis et al. [20,29] suggested yet another hypothesis in which the break was attributed to reconfiguration of single surfactant molecules at the surface. These authors considered that the molecules reconfigured when the interface was covered with a monolayer of the co-polymer to produce a more compact layer at the interface. The decrease in the surface tension after the first break was due to the fact that this compact layer could accommodate more polymer molecules. The decrease in the slope was postulated to be due to slower rate of adsorption after reconfiguration [20].

The surface tension versus concentration profiles in this study also show three distinct breaks for all the surfactants studied (Fig. 5). In order to determine the effect of molecular weight, surface tensions of L-44, L-64 and P-104 series block co-polymers were measured and the results are presented in Fig. 5 (see Table 2 for molecular weights of these surfactants). A detailed discussion on the effect of concentration and molecular weight is given in a later section.

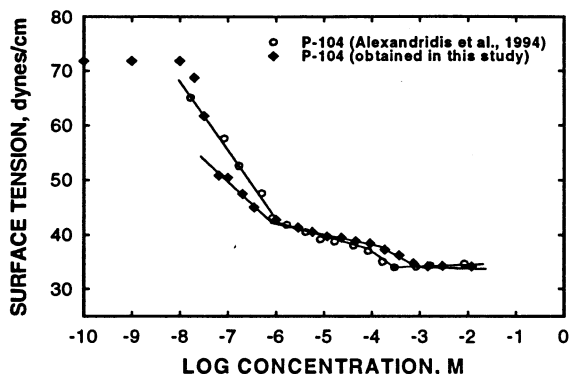


Fig. 4. A comparison of the surface tension data of Pluronic P-104 obtained in this study with that of [20].

### 3.1.3. Effect of ethylene oxide groups

The effect of the hydrophilic portion of the surfactant structure on their surface tension behavior was investigated for L-62 and L-64. The results are presented in Fig. 6 (see Table 2 for the

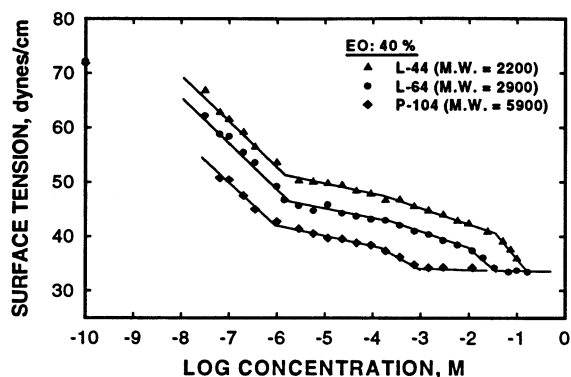


Fig. 5. The surface tension vs. concentration curves for L-44, L-64 and P-104 that demonstrate effect of the molecular weight.

number of EO groups for these surfactants). The data of Alexandridis et al. [20] for P-65 are also included. Within the limits of experimental error, the results were identical, confirming the previous findings that EO groups have a small effect on surface tension.

### 3.2. A hypothesis for the association behavior of triblock co-polymers

Based on the results given in previous sections, a schematic representation of change in surface tension as a function of surfactant concentration is given in Fig. 7. The surface tension behavior

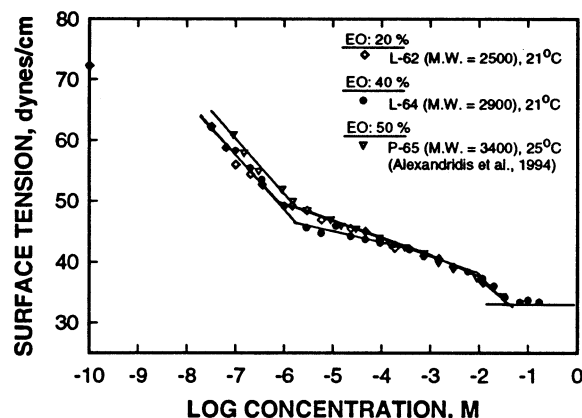


Fig. 6. The surface tension vs. concentration curves for L-62, L-64 and P-65 that demonstrate the effect of the fraction of EO groups.

could be divided into three concentration regions marked as Regions I, II and III. Monomers are considered to be present in Region I, dimers and trimers, etc., in Region II and micelles in Region III. The concentration at which molecules begin to associate is referred to as the critical association concentration (cac).

#### 3.2.1. Region I

All the molecules are considered to be in their monomer form and are expected to adsorb at the air–water interface depending on their surface activity. The adsorption density may be calculated from surface tension data using the Gibbs equation. It is well-known that the Pluronic series of reagents have a broad molecular weight distribution<sup>1</sup> [30] and a distribution of EO and PO groups [10,28]. If one assumes that they are made up of three discrete molecular weights and three discrete PO fraction intervals (high, intermediate and low), such that any molecule would fall into one of the nine molecular weight–PO fraction intervals, the Gibbs adsorption isotherm may be written as follows:

$$d\gamma = -RT \sum_{i=1}^3 \sum_{j=1}^3 \Gamma_{ij} d \log C_{ij} \quad (1)$$

where  $\gamma$  is the surface tension in dynes  $\text{cm}^{-1}$  and  $\Gamma_{ij}$  and  $C_{ij}$  are the adsorption density and the bulk concentration of the component that fall into the  $i$ th molecular weight and  $j$ th PO fraction interval, in  $\text{mol cm}^{-2}$  and  $\text{mol l}^{-1}$ , respectively. It is reasonable to assume that the low molecular weight component of the Pluronics possesses a larger diffusivity and constitutes the main portion of the adsorbing molecules at low concentrations. Then, the adsorption isotherm for Region I can be written as follows:

$$d\gamma = -RT \sum_{j=1}^3 \Gamma_{1j} d \log C_{1j} \quad (2)$$

<sup>1</sup> Polydispersity index, PI, which is a measure of the width of the distribution of molecular weights for a given surfactant, is 1.34 for Pluronic P-104 ([34]). The PI takes values between 1, narrow distributions, and 2, broad distribution. It is defined as the ratio of weight-averaged molecular weight to number-averaged molecular weight of the surfactant molecules.

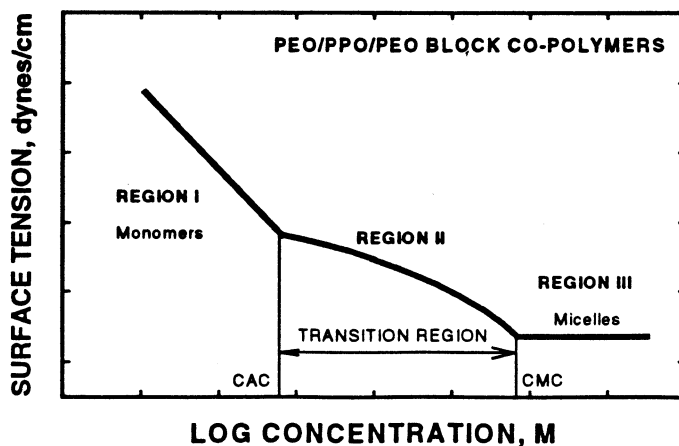


Fig. 7. A schematic diagram of the surface tension vs. concentration profile of PEO–PPO triblock co-polymers.

where  $\Gamma_{ij}$  and  $C_{ij}$  are the surface excess and the bulk concentration of the low molecular weight component that fall into the  $j$ th PO fraction interval, respectively. The area per molecule at the interface,  $A_m$ , can be calculated as:

$$A_m = \frac{1}{\Gamma_m N_{av}} \quad (3)$$

where  $\Gamma_m$  is the surface excess concentration at monolayer coverage and  $N_{av}$  is the Avagadro number. The area calculated provides information on the degree of packing and the orientation of the adsorbed molecule.

From the surface tension values in Region I, the adsorption density was calculated to be  $1.59 \times 10^{-10} \text{ mol cm}^{-2}$  for Pluronic L-64, or a parking area of about  $1.04 \text{ nm}^2$  per molecule. Since the area of a single PO group is  $0.11 \text{ nm}^2$ , and L-64 contains 30 PO groups, the total PO parking area is about  $3.3 \text{ nm}^2$  for the extended molecule. On the basis of these calculations one may consider that the molecules do not adsorb with their extended configuration, only a fraction of PO groups resides at the surface. The hydrophobic portions of these molecules are considered to be in a collapsed form in water by some investigators [30]. Therefore, it is difficult to estimate the number of PO groups attached to the surface.

Since the increase in molecular weight did not change slope of the curve in this region, the area

per molecule,  $1.04 \text{ nm}^2$  at monolayer coverage, should be the same for all three surfactants. Based on these results, one may conclude that only a fraction of the PO groups anchor to the surface and the remainder stay in water. The fraction was about the same for the three surfactants. One may consider that those molecules that adsorb at the interface may be the same component, probably a low molecular weight fraction, for the three surfactants. However, the time to reach equilibrium surface tension was different for these surfactants as shown by the light line in Fig. 8. The time to reach equilibrium is longer for the larger P-104, which suggests that the size of the molecules

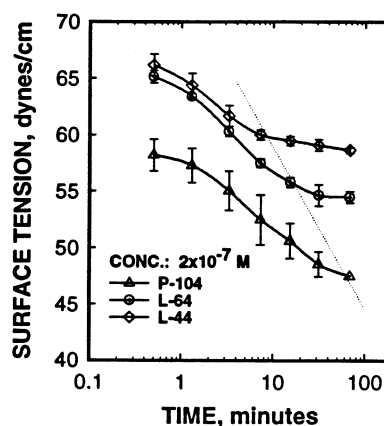


Fig. 8. The effect of conditioning time on the surface tension of Pluronic L-44, L-64 and P-104 surfactants.

adsorbing at the surface is also larger as expected. The time was shorter in the case of smaller L-44 molecules.

The concentration where the first break in the curve occurred was about the same for all the surfactants. That is, the cac is not a strong function of surfactant type. The concentration where the first break in the curve occurred was also found to be independent of temperature and the molecular weight of the block co-polymer by other investigators [20,28]. The surface tension in Region I was a function of surfactant type, and it depended more on the hydrophobic PPO group than the hydrophilic PEO group, as can be seen from Figs. 5 and 6.

### 3.2.2. Region II

This is a transition region between Regions I (monomers) and III (micelles) and covers the concentration range between the cac and the cmc. The presence of such a transition region has caused some confusion in the literature and a satisfactory explanation is still lacking. To explain the results it is reasonable to assume that some of the surfactant molecules will be strongly hydrophobic since they may contain a higher ratio of PO groups due to polydispersity of PO and EO functional groups. This highly hydrophobic material could aggregate at lower concentrations as dimers, trimers, etc. and still adsorb at the air–water interface. The fact that such a transition region is not observed in the case of polydispersed ethoxylated phenols where the polydispersibility is due to ethylene oxide groups supports this hypothesis. Zhou and Chu [10] also state that polydispersity of the insoluble block affects micellization considerably more than that of the hydrophilic block.

The increase in the slope within this region at higher concentrations (which in general is lower than the slope in Region I) is attributed to the re-configuration, hence increased adsorption, of the molecular aggregates at the surface. The transition region became shorter as molecular weight increased due to micelles at lower concentrations, as can be seen on Fig. 5.

### 3.2.3. Region III

In this region, the surface tension became independent of concentration as expected for formation of micelles. The cmc changes as a function of surfactant type and temperature as expected for this type of reagents. The cmc, defined as the concentration for transition between Regions II and III, decreased with an increase in the molecular weight of the surfactants. This is in agreement with the micelle formation behavior of more traditional, monodispersed surfactants, where the critical micelle concentration (cmc) decreases with increasing molecular weight [31,32].

The surface tension behavior of Pluronic-type surfactants, schematically shown in Fig. 7, partly explains the discrepancies in the literature with respect to the cmc of these surfactants. For example, the cmc value observed by light scattering methods (see Table 1) covers a range between  $3.1 \times 10^{-4}$  and  $6.9 \times 10^{-3}$  M in a temperature range of 27–40°C. A plot of the light scattering data as a function of temperature is given in Fig. 9. The cmc value of  $7 \times 10^{-2}$  M at 21°C was taken as the transition between Regions II and III. In contrast, the cmc observed by surface tension studies is much lower and seems to correspond to the cac. These observations confirm the hypothesis that the light scattering studies were able to see only the full grown micelles, but are unable to discern the dimers, trimers, etc. from the monomers. In comparison, the surface tension measurements are more sensitive to the changes in the molecular aggregation and one could detect the formation dimers, trimers etc. However, the reproducibility of the surface tension data obtained from the literature was not very good, most probably due to the time effects that have not been fully recognized in the past.

### 3.3. Wettability of coal

The effect of surfactant concentration, size or molecular weight of the EO and PO groups, and the fraction of the EO groups on wettability in the coal–air–water system was investigated using contact angle measurements. The results are discussed in the paragraphs that follow.



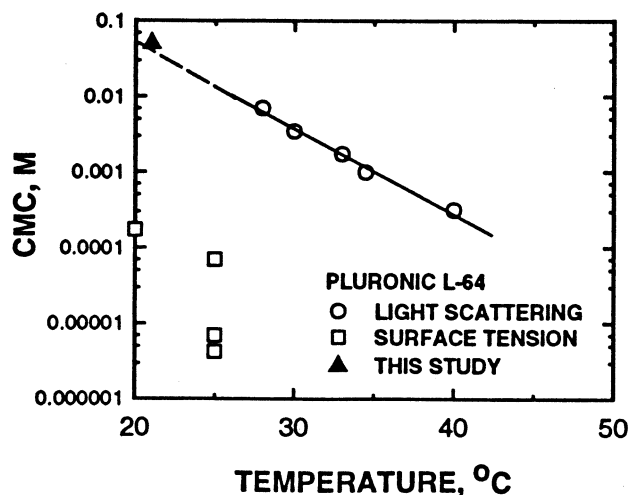


Fig. 9. The effect of temperature on cmc values reported in literature. The data from light scattering and surface tension methods are plotted separately.

### 3.3.1. Effect of block co-polymer concentration

The reproducibility of contact angle measurements on the Pittsburgh coal substrate was determined by conducting replicate tests in the absence of surfactant. It was observed that a normal probability function with a mean contact angle,  $\theta_m$ , of  $47.3^\circ$  and standard deviation,  $\theta_\sigma$ , of 3.3 could be used to approximate all the four distributions (Fig. 10). Hence, only these two parameters,  $\theta_m$  and  $\theta_\sigma$ , will be used hereafter to represent the contact angle distributions. Addition of a block co-polymer changed the contact angle quite significantly as can be seen from the results in Figs. 11 and 12. The effect of concentration was complex and it depended on reagent type. The reasons for such a behavior are not clear but they could be attributed to adsorption of PO groups on hydrophobic sites and EO groups on hydrophilic sites. The reagents L-64 and P-104 gave highest contact angles of  $57.5^\circ$  and  $55^\circ$  in a concentration range from  $10^{-8}$  to  $10^{-6}$  M. The contact angle decreased to zero at higher concentrations, exceeding  $3 \times 10^{-5}$  M. This decrease in contact angle coincided with the critical wetting concentration of these polymers [33].

The standard deviation decreased from 3.3 in distilled water to 2.5 in the surfactant concentration range from  $10^{-7}$  to  $10^{-5}$  M. A somewhat high standard deviation of contact angle was ob-

served in several cases at low reagent concentrations. It was attributed to a site specific adsorption of surfactant molecules on the heterogeneous surface of coal. It is conceivable that PPO groups will adhere to the hydrophobic surface, whereas PEO groups to the hydrophilic surface in such a manner so as to increase the

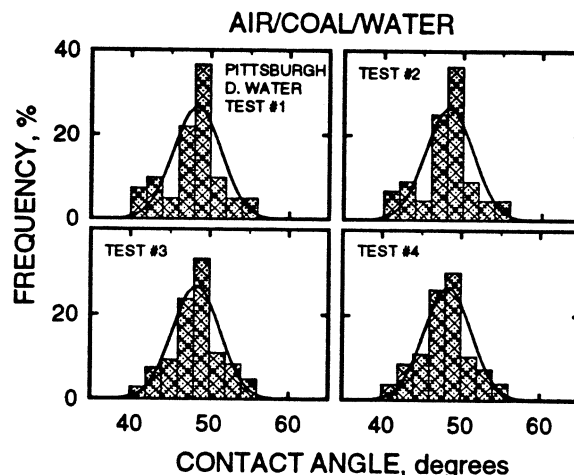


Fig. 10. Contact angle distributions on a Pittsburgh seam sample in distilled water. Test #1, Test #2, Test #3 and Test #4 are repeat tests showing the reproducibility of the measurements. (The normal distribution curves superimposed on the histograms are identical with a mean and standard deviation of  $47.3^\circ$  and  $3.3^\circ$ , respectively)

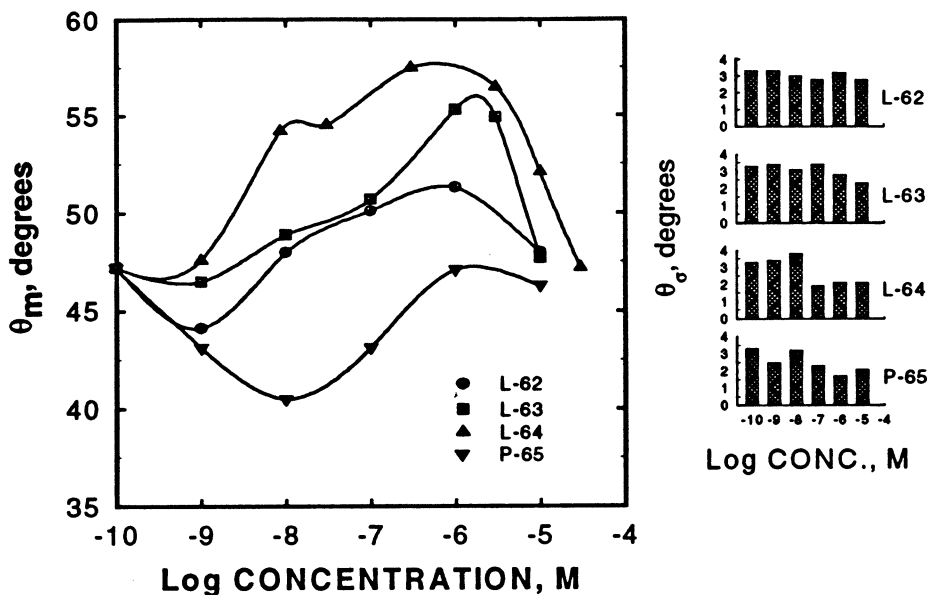


Fig. 11. Effect of ethylene oxide fraction of PEO/PPO/PEO triblock co-polymer on contact angle of Pittsburgh seam sample for the Pluronic-60 series.  $\theta_m$ , mean contact angle;  $\theta_\sigma$ , standard deviation of contact angles about the mean.

apparent heterogeneity of coal. At higher concentrations, the adsorbed surfactant made the surface more homogeneous as more of the surface became covered by the adsorbed reagent. The increase in the contact angle is proposed to result from preferential coverage of the hydrophilic sites by surfactant molecules. To substantiate this hypothesis and to establish an adsorption mechanism additional studies were conducted using polymers with different molecular weights and HLB and the results are discussed in the paragraphs that follow.

### 3.3.2. Effect of ethylene oxide groups

To determine the effect of the ethylene oxide groups on the contact angle two series of reagents were chosen. In the first series, the number of PO groups was 30 and the percent of EO groups increased from 20 to 50 in the reagents L-62, L-63, L-64 and P-65. In the second series, the number of PO groups was 56 and the percent of EO groups increased from 30 to 50 in P-103, P-104 and P-105. The results of these studies are presented in Figs. 11 and 12, respectively. Standard deviations of the contact angle distributions

are given in the right margins. The results show a non-linear relationship between the contact angle and the size of the hydrophilic group. The reagents L-64 and P-104 with an ethylene oxide fraction of 40% were found to be most effective in increasing the contact angle of coal. This suggests that there is an optimum propylene oxide/ethylene oxide ratio that renders the surface most hydrophobic.

### 3.3.3. Effect of molecular weight

A series of reagents containing 40% EO were selected to determine the effect of molecular weight. These reagents were L-44, L-64 and P-104 with molecular weights of 2200, 2900 and 5900  $\text{g mol}^{-1}$ , respectively. The results, presented in Fig. 13, show that Pluronic L-64 and P-104 increased the contact angle from 47 to 57° in the concentration range from  $10^{-8}$  to  $10^{-6}$  M. The reagent Pluronic L-44, increased the contact angle only slightly, from 47.3–51°.

### 3.3.4. Contact angle and HLB value

To determine the effect of HLB on the contact angle it was necessary to select an appropriate

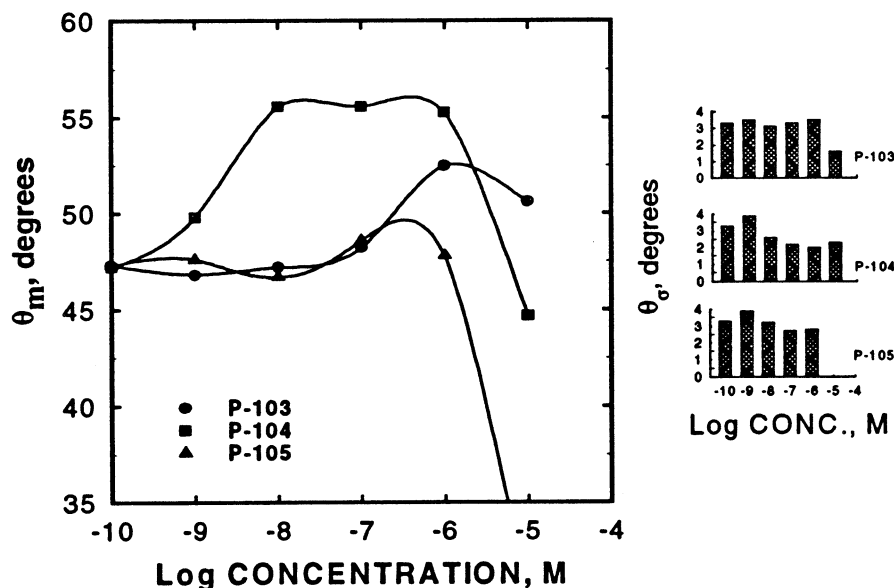


Fig. 12. Effect of ethylene oxide fraction of PEO/PPO/PEO triblock co-polymer on the mean contact angle ( $\theta_m$ ) of Pittsburgh seam sample for the Pluronic-100 series.

concentration. For this purpose, the maximum value of the contact angle was selected from the contact angle versus concentration data, and the results are plotted in Fig. 14. The contact angle was maximum at an HLB values of 14 for the series-60 reagents, and it was 15 for the series-100 reagents. These results show that both reagent type and concentration are important for obtaining the most hydrophobic surface. The standard deviations of the contact angle distributions are also given, as error bars. These results show that the effect of HLB is statistically significant because the change in contact angle is much larger than the standard deviation.

### 3.4. A hypothesis for adsorption of triblock co-polymers on coal

There is a general agreement in the literature that adsorption of PPO/PEO block co-polymers occurs on a hydrophilic surface through ethylene oxide groups, possibly involving hydrogen bonds [16,18,22]. In the case of a hydrophobic surface, it occurs via the hydrophobic portion of the molecule exposing PEO groups to the bulk solu-

tion [14,16]. Since the coal surface is known to consist of a mixture of both hydrophilic (methoxy, hydroxy, carboxyl, carbonyl) and hydrophobic (paraffin, graphite, naphthalene) groups, adsorption through both mechanisms is possible. If one considers surface tension and contact angle data for the series-60 reagents, Figs. 6 and 11, it may be concluded that changes in contact angle arise from differences in adsorption of the reagents at the coal surface Fig. 15. The reagent L-62, which contained the least amount of EO groups, most likely adsorbed through the PPO groups and the contact angle decreased at lower concentrations. The reagents L-63 and L-64, containing a greater percentage of EO groups adsorbed probably through PEO groups, increasing contact angle. If the percentage of EO groups was 50%, e.g. in the case of L-65 and P105, the adsorption was such that the contact angle was always the same or lower. These results show that the contact angle for coal is determined by relative adsorption of the reagents at both the hydrophobic and the hydrophilic sites. Obviously, more studies are needed to confirm this hypothesis.

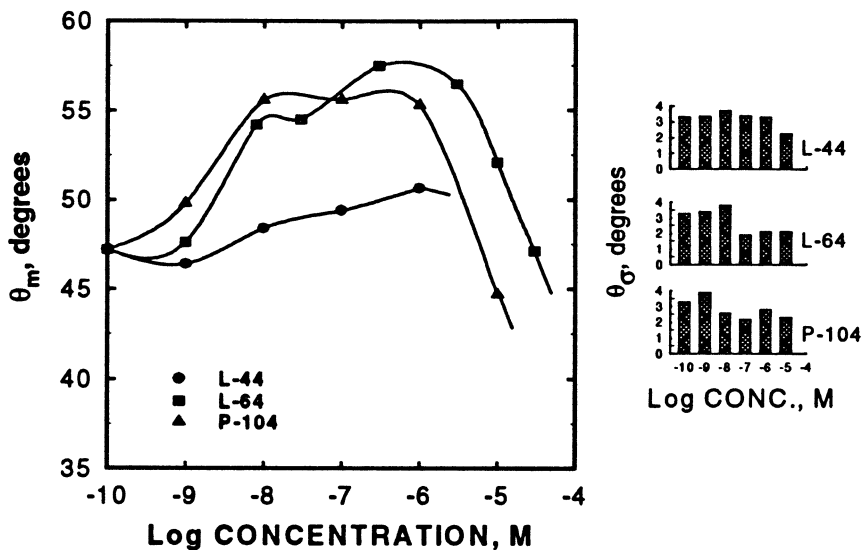


Fig. 13. Effect of molecular weight of the PEO/PPO/PEO triblock co-polymers on the mean contact angle ( $\theta_m$ ) of Pittsburgh seam coal.

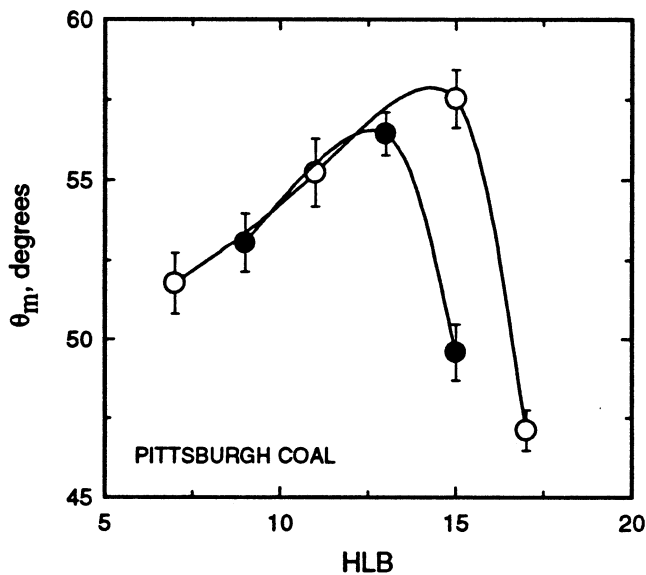


Fig. 14. Effect of HLB on contact angle of Pittsburgh seam sample for two different series of Pluronic surfactants. ●, 60-series; ○, 100-series;  $\theta_m$ , mean contact angle.

#### 4. Conclusions

Adsorption of PEO/PPO/PEO triblock co-polymers at the liquid–air interface and their effect on wetting of coal was investigated in this study. The

following conclusions may be made:

1. Several minutes to about 1 h was needed to reach equilibrium at the liquid–air interface.
2. Three distinct regions in the surface tension versus concentration profiles were observed:

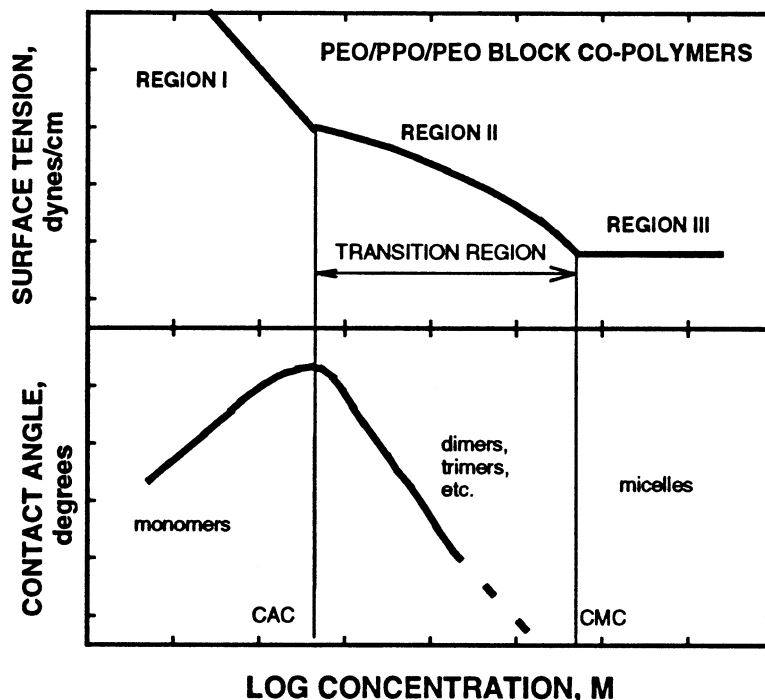


Fig. 15. A schematic diagram that shows the relationship between the surface tension behavior of the triblock co-polymers and the contact angles on coal in their presence.

(1) In Region I, the molecules were present as monomers. This region extended from low concentrations to a concentration where molecules began to associate. This concentration is referred to as critical association concentration (cac).

(2) In Region II, at concentration above the cac, the molecules are proposed to be in the form of dimers, trimers, etc. The slope of the surface tension curve was lower than that in Region I, but increased gradually with an increase in concentration, most probably due to reconfiguration of the associated molecules at the surface.

(3) In Region III, micelles formed at concentrations above the cmc.

3. At low concentrations, most of the triblock co-polymers used in this study increased the hydrophobicity of coal. The contact angle increased with reagent concentration, reaching a maximum at the cac. Under these conditions, adsorption was postulated to occur through PEO groups on the hydrophilic sites. When the adsorption of

PEO dominates, PPO groups would be exposed resulting in an increase in contact angle. In some cases, the contact angle decreased in the presence of the reagent. It was postulated that adsorption in these cases occurred through PPO groups on the hydrophobic sites. The exposed PEO groups rendered the surface more hydrophilic.

4. Above the cac, the molecules started to associate through PPO groups to form dimers, trimers, etc., and the contact angle decreased.

5. The contact angle decreased precipitously at concentrations above the cmc due to formation of surface micelles or adsorption of micelles at the surface.

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