Contrasts in the Surface Activity of Polyoxypropylene and Polyoxybutylene-Based Block Copolymer Surfactants

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ABSTRACT: Previous studies have shown that polyoxybutylene surfactant hydrophobes are less polar than polyoxypropylene hydrophobes. Polyoxyalkylene hydrophobes can be modified by ethoxylation to give terminal polyoxyethylene block hydrophilic groups. Polyoxybutylene/polyoxyethylene copolymer surfactants exhibit differentiated interfacial tensions, and wetting and foaming properties when compared to structurally equivalent polyoxypropylene/polyoxyethylene copolymers. There have been no reported comparisons, however, of polyoxybutylene/polyoxyethylene copolymers and polyoxypropylene/polyoxyethylene analogues in terms of fundamental parameters, such as critical micelle concentration, area per molecule at the interface, efficiency, and effectiveness. In one phase of this work, four polyoxybutylene/polyoxyethylene block copolymer surfactants were compared to structurally analogous polyoxypropylene/polyoxyethylene materials. Findings showed that polyoxybutylene/polyoxyethylene copolymers exhibited enhanced cotton wetting and lower surface and interfacial tensions compared to polyoxypropylene/polyoxyethylene analogues. Polyoxybutylene-based surfactants were typically one order of magnitude better in their ability to reduce surface tension at interface saturation. Polyoxybutylene/polyoxyethylene copolymers pack more efficiently at the interface, as evidenced by a smaller area per molecule at the interface. Critical micelle concentration values were also lower for polyoxybutylene/polyoxyethylene copolymers. A second phase of experiments focused on the surface activity of polyoxypropylene/polyoxyethylene triblock copolymers with higher molecular weight hydrophobes. Enhanced surface activity was found when compared to lower–molecular weight polyoxypropylene/polyoxyethylene copolymers.

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KEY WORDS: Critical micelle concentration, effectiveness, efficiency, interfacial tension, nonionic surfactant, polyoxybutylene, polyoxyethylene, polyoxypropylene, surface tension, wetting.

Block copolymer nonionic surfactants, made from 1,2-butylene oxide (BO), propylene oxide (PO), and ethylene oxide (EO), are an interesting class of materials. Studies on phase behavior (1,2), gelation (3), micellization (4–6), and microviscosity (7) have recently appeared in the literature, joining hundreds of others on the general subject. Structurally, the hydrophobic blocks consist of either a polyoxypropylene (POP) or polyoxybutylene (POB) homopolymer. One or more polyoxyethylene (POE) homopolymer blocks make up the hydrophilic moiety of the surfactant. Previous results from this laboratory, dealing with structure/property relationships of these copolymers, have been reported (8).

Inverse gas-chromatographic studies (9) have shown that the polarity of the POP hydrophobe is greater than that of POB. It is generally known that POP homopolymers are more water-soluble and less oil-soluble than POB homopolymers (10). This is not surprising in view of the difference in the weight percentage oxygen content between POP and POB polymers, with POP having more oxygen.

Variation of initiator functionality (monol, diol, triol, and so forth) as well as the order of oxide addition can lead to surfactants with a wide range of properties and structure. In this study, initiator functionality was limited to monols and diols, giving diblock and triblock copolymers, respectively. In the case of monol-initiated diblock copolymers, oxide addition was performed in two ways, that is, BO (or PO) followed by EO, or EO followed by BO (or PO). Figures 1 and 2 show simplified block models of the surfactants used for this work.

Initial data generated in this laboratory have shown that POP/POE block copolymer surfactants, as a class, exhibit lower surface activity than do POB/POE polymers. A good synopsis of polyoxyalkylene block copolymer properties has been offered (11,12). A survey of the literature, however, has found no manuscripts that deal directly with performance

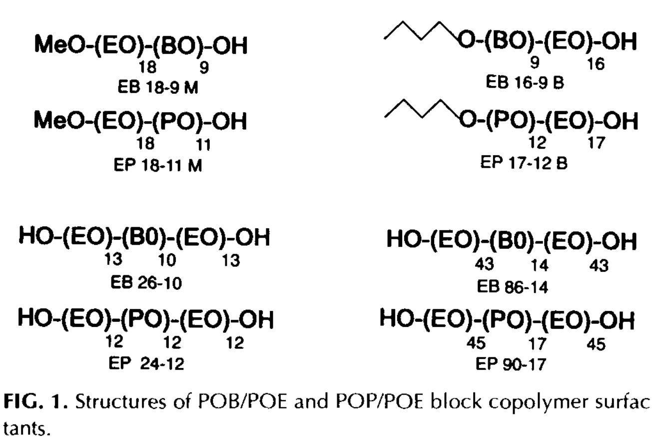

FIG. 1. Structures of POB/POE and POP/POE block copolymer surfactants.

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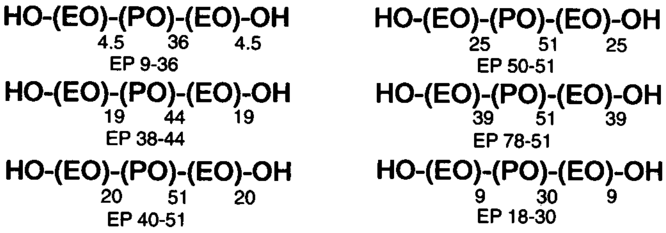

$HO\text{-}(EO)_{4.5}\text{-}(PO)_{36}\text{-}(EO)_{4.5}\text{-}OH$ EP 9-36

$HO\text{-}(EO)_{19}\text{-}(PO)_{44}\text{-}(EO)_{19}\text{-}OH$ EP 38-44

$HO\text{-}(EO)_{20}\text{-}(PO)_{51}\text{-}(EO)_{20}\text{-}OH$ EP 40-51

$HO\text{-}(EO)_{25}\text{-}(PO)_{51}\text{-}(EO)_{25}\text{-}OH$ EP 50-51

$HO\text{-}(EO)_{39}\text{-}(PO)_{51}\text{-}(EO)_{39}\text{-}OH$ EP 78-51

$HO\text{-}(EO)_{9}\text{-}(PO)_{30}\text{-}(EO)_{9}\text{-}OH$ EP 18-30

FIG. 2. Structures of high-molecular weight POP/POE block copolymers.

comparisons of these two classes of polyoxyalkylene block copolymer surfactants.

This paper presents a detailed comparison of POB/POE and POP/POE block copolymer surfactants in terms of several key interfacial performance parameters, such as surface and interfacial tensions, critical micelle concentration (CMC), area per molecule at the interface, wetting, and foaming. In one set of experiments, four commercial POB/POE block copolymer surfactants were compared to POP/POE copolymers of analogous block structure and molecular weight (Fig. 1). A second set of experiments dealt with the performance properties of POP/POE triblock diols with high-molecular weight POP hydrophobes (Fig. 2). Structures of the higher–molecular weight copolymers were chosen from a review of the best tertiary literature references available on their properties (11,12).

EXPERIMENTAL PROCEDURES

POB/POE block copolymers. Commercial POB/POE materials, designated as BM45-1600, BL50-1500, B40-1900, and B20-5000, were obtained from Dow Chemical Co. (Midland, MI) and were used without further modification. As represented in this work, the materials are named EB 18-9 M, EB 16-9 B, EB 26-10, and EB 86-14, respectively. In this system of nomenclature, the first number refers to the average number of EO units in the molecule, and the second represents the average number of butoxy groups in the hydrophobe (Fig. 1). Suffixes "M" and "B" refer to methyl and *n*-butyl termination, respectively.

POP/POE block polymerization reactions. All POP/POE polymerizations were run in steel closed-system reactors. Initiators for POP/POE diblock monol syntheses were propylene glycol *n*-butyl ether (DOWANOL™ * PnB) and diethylene glycol monomethyl ether (DOWANOL* DM) (both from Dow Chemical Co.). POP/POE triblock diols were initiated with 1,2-propylene glycol (Dow Chemical Co.). Solid potassium hydroxide (KOH) (Fisher Scientific Co., Fair Lawn, NJ) was used as the alkoxylation catalyst at concentrations of 6% (w/w) for 1,2-propylene glycol and 2% (w/w) for monol initiators. Control temperature for oxide additions was 130°C. KOH catalyst, remaining in the final products, was neutralized with a molar equivalent of glacial acetic acid (Fisher Scientific Co.). Other specific aspects of the POP/POE block polymerization reactions have been presented in a previous work (8). Nomenclature for POP/POE copolymers is identical to that described above for POB/POE materials, except the second number refers to the average number of PO monomer units in the hydrophobe (Fig. 2).

Percent hydroxyl analysis. Hydroxyl analysis for determining number-average molecular weights was performed with test method ASTM D 4274-88, method D, with the modification in which endpoints were detected by potentiometry (13). All structures in Figures 1 and 2 were obtained by this analysis.

Draves wetting time. The method used was taken from ASTM D 2281-68 (13). A 3-g copper hook was used. The cotton test skeins were purchased from Testfabrics, Inc. (Middlesex, NJ). Three surfactant concentrations were used to study the high–molecular weight POP/POE copolymers. Lower–molecular weight copolymers were run at 1.0% (wt/vol) only.

Ross–Miles foam testing. ASTM method D 1173-53 was used (13). A jacketed foam receiver was first thoroughly cleansed with Nochromix agent (Godax Laboratories, Inc., Pawling, NY) and rinsed three times with tap water, followed with deionized water. A temperature-controlled bath maintained temperature at specified set points. Foam tests were carried out at concentrations of 0.1 and 1.0 (wt/vol) percent.

Surface tension and other interfacial property measurements. A Krüss model K-12 computer-automated tensiometer (Krüss, Charlotte, NC) was used to measure all surface and interfacial tensions. Interfacial tensions were run under *n*-dodecane (Aldrich, Milwaukee). Krüss system accessories included a constant-temperature circulating bath, which held the temperature at 25°C ± 0.1°C, and an automated pipette dispenser for dosing precise increments of the appropriate surfactant stock solution into the measuring vessel for CMC determinations. A logarithmic dosing method was used. Interfaces were not aged to any given degree other than the time needed for the instrument to take measurements.

Cloud point. Approximately 80 mL of a 1% (wt/vol) surfactant solution was added to a 100-mL beaker equipped with a magnetic stirrer. The solution was placed atop a heater/stirrer unit. A red-alcohol thermometer bulb was immersed fully into the solution and clamped to a ring stand. Heating was gradually increased to give a solution temperature rise of approximately 2°C per min. Two observations were made: (i) temperature at which the solution first became turbid, and (ii) temperature at which the turbidity completely obscured the thermometer bulb from view. Cloud points reported as being below or near 25°C were run by first cooling the solution to about 5°C and allowing the solution to warm slowly.

RESULTS AND DISCUSSION

Comparison of low–molecular weight POP/POE copolymer performance to analogous POB/POE Systems. Figure 1 shows the structures of surfactants used in this series of experiments. In this figure and elsewhere in the paper, POB/POE and POP/POE copolymers are designated by the

TABLE 1
Draves Wetting Performance for POB/POE and POP/POE Block Copolymer Analogues

Copolymer surfactant	Draves wetting time (s, 1.0%)	Wt% ethylene oxide
EB 18-9 M	2	55
EP 18-11 M	>360	56
EB 16-9B	4	49
EP 17-12 B	>360	49
EB 26-10	0	60
EP 24-12	>360	60
EB 86-14	>360	79
EP 90-17	>360	80

"EB" and "EP" nomenclature described previously. The four POB/POE copolymers were chosen based on their structural diversity in terms of functionality, block structure, and percentage of EO. For each of the four POB/POE copolymers, a POP/POE analogue was made. These analogues were targeted to have the same hydrophobe and hydrophile block molecular weights, and therefore the same weight percentage of PEO hydrophile. The set of POP/POE copolymers could be described as having molecular weight equivalency with the POB/POE copolymers.

Cotton wetting performance. Table 1 summarizes the Draves wetting comparisons for copolymer pairs shown in Figure 1. Draves wetting times for POP/POE copolymers are always greater than 6 min, thus illustrating very slow wetting. Comparing this performance to POB/POE materials, which exhibit lower wetting times, it is evident that POP/POE analogues do not perform equally. EB 86-14 is an exception due to high EO content.

POB/POE copolymers wet cotton more efficiently than POP/POE analogues because of the oillike nature of the POB hydrophobe and its ease of interface formation with hydrophobic cotton fibers. Under the conditions of the test, POP/POE copolymers do not wet the test skein at the same rate as do POB/POE materials in a kinetic sense. Over time, however, wetting may eventually occur and reach interfacial equilibrium.

Foaming properties. Ross–Miles foam testing was performed on the eight surfactants described in Figure 1. Table 2 shows the results of the testing with 0.1% and 1.0% solutions of surfactant at 25 and 50°C. Overall, the POP/POE copolymers were lower-foaming than their POB/POE counterparts due to a more stable liquid–air interface. Foam stability was calculated as the percentage of foam remaining after 5 min with respect to the initial foam height. The following items (i)–(iv) are descriptions of data for each group of surfactants:

(i) *EB 18-9 M and EP 18-11 M.* At 0.1% and 25°C, foaming level and stability for EB 18-9 M was much higher than for EP 18-11 M. EP 18-11 M showed zero foam stability after 5 min. At 1.0% and 25°C, foaming was higher for EB 18-9 M and had greater stability. Initial foaming for EP 18-11 M at 1.0% was lower compared to 0.1% concentration, and again had zero stability. At 50°C, EB 18-9 M behaved similarly to the 25°C determination at both concentrations, except for greatly decreased foam stability. For EP 18-11 M, foaming was reduced or eliminated at 50°C due to being run at the cloud point;

(ii) *EB 16-9 B and EP 17-12 B.* EB 16-9 B exhibited initial foam heights similar to EB 18-9 M throughout the concentration and temperature range. Unlike EB 18-9 M, however, foam stability was not greatly affected by a temperature increase from 25 to 50°C. EP 17-12 B was lower-foaming overall when compared to EB 16-9 B.

(iii) *EB 26-10, and EP 24-12.* Again, the POP/POE analogue was lower foaming than the POB/POE copolymer. Initial foam heights for both surfactant types increased with increasing concentration. Temperature change from 25 to 50°C did not appreciably change the foaming properties or foam stability of both copolymers.

(iv) *EB 86-14 and EP 90-17.* EB 86-14 generated highly stable foams at 25°C for both concentrations. At 50°C initial foam heights at both concentrations were similar to those run at 25°C, but stability was greatly diminished. EP 90-17 generated similar initial foam levels at both concentrations measured at 25°C. The stability decreased at the 1% concentration, however. At 50°C, the initial foam was about 20 mm lower for both concentrations compared to 25°C, and stability was decreased at the higher concentration.

Interfacial properties of POB/POE and POP/POE copolymers. To help determine why POB/POE and POP/POE

TABLE 2
Ross–Miles Foam Data for POB/POE and POP/POE Block Copolymer Analogues

Copolymer surfactant	Foam height, $t = 0$, $t = 5$ (0.1%, mm, 25°C)	Foam stability ($t = 5/t = 0$) × 100 % (0.1%, 25°C)	Foam height, $t = 0$, $t = 5$ (1.0%, mm, 25°C)	Foam stability ($t = 5/t = 0$) × 100 % (1.0%, 25°C)	Foam height, $t = 0$, $t = 5$ (0.1%, mm, 50°C)	Foam stability ($t = 5/t = 0$) × 100 % (0.1%, 50°C)	Foam height, $t = 0$, $t = 5$ (1.0%, mm, 50°C)	Foam stability ($t = 5/t = 0$) × 100 % (1.0%, 50°C)
EB 18-9 M	116, 70	60	194, 152	78	106, 19	18	191, 27	14
EP 18-11 M	21, 0	0	15, 0	0	8, 0	0	0, 0	0
EB 16-9 B	91, 33	36	169, 33	20	92, 15	16	158, 22	14
EP 17-12 B	32, 12	38	49, 19	39	37, 9	24	—	—
EB 26-10	71, 21	30	170, 18	11	81, 11	14	171, 10	6
EP 24-12	63, 4	6	92, 6	6	56, 8	14	62, 4	6
EB 86-14	101, 95	94	185, 165	89	117, 70	60	172, 81	47
EP 90-17	82, 22	27	84, 5	6	60, 12	20	64, 6	9

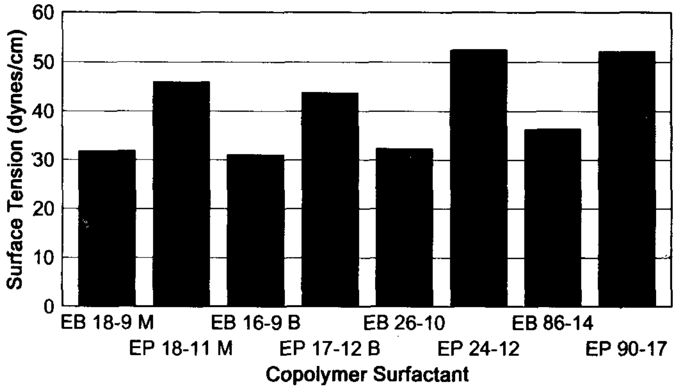

FIG. 3. Aqueous surface-tension measurements of POB/POE and POP/POE copolymer surfactant analogues.

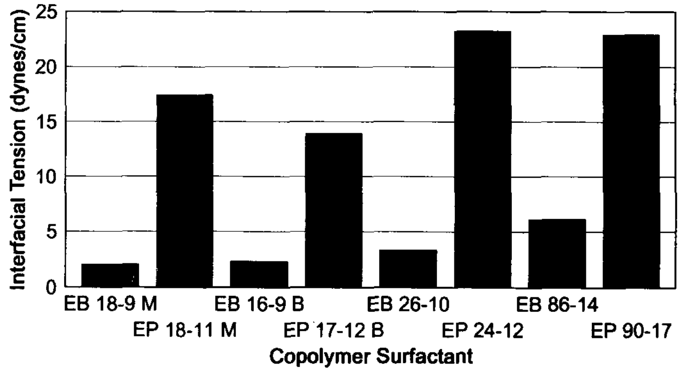

FIG. 4. Interfacial-tension values for POB/POE and POP/POE block copolymers against *n*-dodecane.

copolymer surfactants differ in performance, the nature of the interface was studied by surface-tension analysis. Figures 3 and 4 illustrate surface tension (aqueous/air) and interfacial tension (aqueous/*n*-dodecane) values for the four sets of surfactants at 0.1 wt %. Interfaces were aged for approximately 30 min. Surface-tension values (Fig. 3) for the POB/POE series were 40–60% lower than for POP/POE analogues. Interfacial tension (Fig. 4) was 300–700% lower for POB/POE copolymers. This was not surprising in light of enhanced oil solubility of POB vs. POP homopolymers. Surfactants that contain the POB hydrophobe form a lower-energy interface with nonpolar phases because of increased oil-like polarity. As will be discussed later, POP/POE copolymers do not pack at the interface as tightly when compared to POB/POE counterparts.

Table 3 summarizes data derived from CMC determinations. Raw data were taken by measuring the surface tension in dynes/cm at increasing concentrations and then plotted as surface tension vs. $\log_{10}$ of molar concentration (14). Figure 5 shows a schematic diagram of a typical "bilinear" CMC curve with variables highlighted that can be obtained from the data.

Standard free energy of micellization (15) was calculated with equation [1], where ΔG°_{MIC} is the free energy of micellization in joules/mole; R is 8.31 joules/mole K; T is in degrees Kelvin; CMC is in moles/L; and ω is the molarity of water (55.3 molar at 25°C).

$$\Delta G^\circ_{MIC} = 2.3RT\log(CMC/\omega) \qquad [1]$$

Surface-excess concentration (16) was obtained from equation [2], where Γ is the surface-excess concentration in mole/cm^2, R is 8.31×10^7 ergs/mole K; and T is in degrees Kelvin. The partial differential term, evaluated at constant temperature, is simply the slope of the linear portion of the CMC curve plotted in dynes/cm vs. $\log_{10}$ molar concentration.

$$\Gamma = [-1/(2.3RT)](\partial\gamma/\partial \log C)_T \qquad [2]$$

Area per molecule at the interface (17) resulted from Equation 3, where a is in square angstroms; Γ is in moles/cm^2, and N is Avogadro's number:

$$a = 10^{16}/(N\,\Gamma) \qquad [3]$$

Maximum surface pressure at CMC, or Π_{CMC}, relates to the effectiveness of a given surfactant (18). The value indicates the maximum lowering of surface tension compared to the surface tension of the solvent that contains no surfactant.

TABLE 3
Interfacial Performance Data Comparing POB/POE and POP/POE Block Copolymer Surfactants

Copolymer surfactant	CMC[a] (mg/L)	CMC (molar)	Surface excess (moles/cm^2, E-10)	Area per molecule (Å^2)	ΔG°_{MIC} (kJ/mole)[b]	CMC/C$_{20}$	pC$_{20}$	Maximum surface pressure (dynes/cm)
EB 18-9 M	35	2.3 E-5	2.2	75	−36.4	29.6	6.1	40
EP 18-11 M	90	6.0 E-5	1.2	136	−34.0	7.2	5.1	26
EB 16-9 B	18	1.2 E-5	3.3	51	−37.9	15.1	6.1	41
EP 17-12 B	611	4.1 E-4	0.8	219	−29.3	81.9	5.3	28
EB 26-10	380	2.1 E-4	1.6	103	−30.9	163.7	5.9	40
EP 24-12	899	5.0 E-4	0.5	306	−28.8	0.9	3.3	20
EB 86-14	190	4.0 E-5	1.6	107	−35.0	75.9	6.3	36
EP 90-17	411	8.2 E-5	0.5	323	−33.2	0.4	3.7	20

[a] CMC = Critical micelle concentration.
[b] ΔG°_{MIC} = Free energy of micellization in kilojoules/mole.

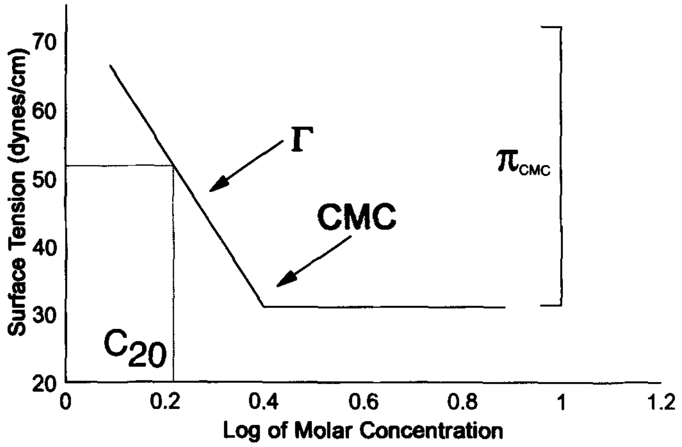

FIG. 5. Schematic diagram of a typical CMC bilinear curve showing derivable variables: Γ = surface excess concentration, CMC = critical micelle concentration, Π_{CMC} = maximum surface pressure, C_{20} = surfactant efficiency.

The efficiency of a surfactant is defined as the concentration needed to produce a given change in surface tension of the solvent. It has been proposed (19) that a surfactant concentration affecting a 20 dynes/cm decrease in surface tension (C_{20}) is a valid measure of efficiency. For essentially all surface-active agents, the interface is over 90% saturated at this point. This is typically a small concentration and is conveniently reported as the negative of the common log of C_{20}, or pC_{20}.

Surface-tension values at 0.1% were used as the lower limit in determining the CMC and maximum surface pressure. Surface-tension values at higher concentrations were essentially constant. That is, little if any decrease in surface tension was noted above this concentration.

CMC evaluations. Table 3 lists the CMC values both in units of weight percentage and molar concentration. Lower CMC values generally indicate that interfacial saturation occurs at lower concentrations, thus suggesting surfactant efficiency. POB/POE surfactants form micelles at lower concentrations than do POP/POE analogues.

The CMC of EP 17-12 B was about seven times higher than that of EP 18-11 M. This may be attributable to the nonpolar *n*-butyl termination on the POP hydrophobe acting to destabilize the higher-polarity micellar POP interior, resulting in a higher CMC. More will be said about endgroup effects later in the paper.

Surface-excess concentration and area per molecule at the interface. As described earlier, surface-excess concentration Γ is a function of the slope of the linear portion of a CMC curve (Fig. 5), and gives the number of moles of surfactant covering 1 cm^2 of interface. Surface-excess concentration can be converted to the area that one molecule of surfactant occupies at the interface. Area per molecule (APM) values therefore help describe the manner in which surfactant molecules arrange or pack at the interface. Table 3 lists surface excess and APM data for the four surfactant pairs. EB 18-9 M has a value of 75. The corresponding copolymer analogue EP 18-11 M occupies about twice as much space at the interface, perhaps due to the POP hydrophobe being more hydrated and less compact. In the case of EB 16-9 B and its analogue EP 17-12 B, APM is smaller by about a factor of 4. EB 26-10 and EB/86-14 have similar APM values, and the corresponding POP/POE analogue triblock diols require about three times more room at the interface. Water solubility and polarity differences between the POP and POB hydrophobes are certainly a factor in interfacial architecture.

Free energy of micellization. The change in system free energy upon micellization is a function of the CMC, as shown in Equation 1. The free energy change becomes greater as the CMC decreases. Micellization is a spontaneous process, and therefore, the free energy change is negative, as shown for the surfactants in Table 3.

For POB/POE copolymers, the most spontaneous micelle formers are the two diblock monols (EB 18-9 M and EB 16-9 B). For each set of two copolymer types, the free energy increases (CMC increases) when the hydrophobe consists of POP.

The negative values of free energy of micellization are driven mainly from large entropy term increases. Micellization increases entropy of the system and corresponds to enthalpy changes of only about –4 to +9 kJ/mole for aqueous nonionic surfactants (20).

Table 3, shows that pC_{20} efficiency values for POB/POE copolymers studied in this experiment generally are 1–2 orders of magnitude higher when compared to POP/POE analogues. Values above 6 are considered to represent high efficiency and correspond to concentrations of 1–2 mg/L.

Surfactant effectiveness, maximum surface pressure. Values of maximum surface pressure (Π_{CMC}) in Table 3 show POB/POE copolymers to be 15–20 dynes/cm more effective in lowering surface tension than corresponding POP/POE analogues. That is, the CMC occurs at a lower surface tension for these POB/POE block copolymers.

CMC/C_{20} ratio. A change in the CMC/C_{20} ratio is most meaningful when studying the effects of discrete structural changes within a particular surfactant class (21). Table 3 lists the CMC/C_{20} ratios for the surfactants studied. An increase in the ratio can mean that either micellization is inhibited more than absorption at the interface or that adsorption at the interface is facilitated more than micellization. A decrease in the ratio can mean that either interfacial absorption is inhibited more than micellization or that micellization is facilitated more than interfacial absorption.

When either the CMC or C_{20} remains essentially constant, and the CMC/C_{20} ratio increases or decreases, conclusions may be drawn as to which inhibition or enhancement is taking place due to a particular structural change. From these data, two pairs of materials can be further studied in terms of structural effects. In the first set considered, EB 18-9 M and EB 16-9 B, the C_{20} values are identical, but the CMC values are different. For this pair of POB/POE diblock monols, CMC/C_{20} values decrease in going from EB 18-9 M to EB 16-9 B. This could mean either that absorption at the interface is inhibited more than micellization or that micellization is facilitated more than absorption. Seeing that absorption does not change with the structural change (both pC_{20} values are 6.1), it follows that the structural changes facilitate micellization.

The second set consists of two POP/POE diblocks, EP 18-11 M and EP 17-12 B. In this case, however, the CMC/C_{20} ratio increases (Table 3), while the pC_{20} remains essentially constant. This is an opposite effect compared to the POB/POE copolymer set. Therefore, the structural changes inhibit micellization.

One plausible approach to explain these differences in micellization would be to evaluate the hydrophobe endgroup effects in the interior of the micelle. Scheme 1 summarizes the analysis of endgroup effects for these two sets of diblock copolymers.

Internal micellar phase with POB and *n*-butyl group terminus (like solubilities) favors micellization with respect to POB with OH terminus.

Internal micellar phase with POP and *n*-butyl group terminus (unlike solubilities) disfavors micellization with respect to POP with OH terminus.

SCHEME 1

For the POB/POE diblock monols, it may be thermodynamically unfavorable for the highly polar terminal hydroxyl groups to exist in the nonpolar POB micellar interior (EB 18-9 M). The POB hydrophobe, containing *n*-butyl ether (EB 16-9 B) as the endgroup, would tend to alleviate this polarity difference and facilitate micellization.

Again referring to Scheme 1, the *n*-butyl ether moiety on the POP/POE analogue hydrophobe (EP 17-12 B) may be too nonpolar to be easily miscible with the relatively polar POP polymer. The surfactant with the hydroxyl endgroup on the POP hydrophobe (EP 18-11 M) micellizes at lower concentration and perhaps indicates that the hydroxyl terminus is more compatible with the POP internal phase.

Cloud-point measurements. Data in Table 4 indicate an overall trend higher in cloud point for POB/POE diblock materials. This could be due to dissimilar hydration of POP and POB blocks, causing greater temperature sensitivity. Cloud points for EB 26-10 triblock and the POP/POE analogue are not different enough to offer much discussion. Nonionic surfactants with a POE content of 80% or greater (EB 86-14 and EP 90-17) are soluble up to 100°C and therefore do not show a cloud point.

TABLE 4
Cloud-Point Behavior of POB/POE vs. POP/POE Block Copolymer Surfactants

Copolymer surfactant	Cloud point, initial (°C)	Cloud point, final (°C)
EB 18-9 M	48	57
EP 18-11 M	40	50
EB 16-9 B	63	99
EP 17-12 B	37 (48) 58	63
EB 26-10	79	81
EP 24-12	82	85
EB 86-14	[a]	[a]
EP 90-17	[a]	[a]

[a] No cloud point seen at or below 100°C.

EP 17-12 B POP/POE monol exhibits a "double cloud point." The 1% solution first shows cloudiness at 37°C, reverts to a clear solution at 48°C, and begins to cloud again at 58°C, finally followed by complete solution opacity at 63°C. The double–cloud-point phenomenon may be due to resolubilization of the initial condensed phase at a higher temperature followed by complete phase-out of surfactant aggregates.

Results and discussion for property determinations focusing on high-molecular weight POP/POE block copolymer surfactants. Six POP/POE triblock diols (Fig. 2) were studied in a similar fashion to those just mentioned. Note here that the hydrophobe molecular weights are much higher compared to the previous set of surfactants. Also note that the hydrophile content is lower overall. POB/POE copolymers in this range of molecular weight and hydrophile percentage are not appreciably water-soluble due to the low-polarity POB hydrophobe. The purpose of this part of the investigation was to demonstrate that high–molecular weight POP hydrophobes in POP/POE block copolymers could impart increased surface activity, approaching that of lower–molecular weight POB/POE materials.

Cotton wetting performance. Draves wetting data are summarized in Table 5. Good wetting was seen with all materials, and copolymers with a 3,000-Mw POP hydrophobe performed the best. EP 9-36 had a cloud point below 25 °C for 1.0 and 0.5% concentrations.

Foaming properties. For POP/POE copolymers, an increase in surface activity led to increased foaming ability. Table 5 lists the Ross–Miles foam height data for two surfactant concentrations, each at 25 and 50°C. Most of the foam values were similar to, and in some cases exceeded, those for lower–molecular weight POB/POE materials discussed previously. EP 9-36 and EP 18-30 were lower foamers.

Surface tension. Surface-tension values for 0.1% solutions are listed in Table 5. The lowest values were shown by the

TABLE 5
Wetting, Foaming, and Surface-Tension Data for High-Molecular Weight POP/POE Block Copolymer Surfactants

Copolymer surfactant	Draves wetting time (s, 0.1, 0.5, and 1.0%	Foam height, $t = 0$ $t = 5$ (0.1%, mm, 25°C)	Foam height, $t = 0$ $t = 5$ (1.0%, mm, 25°C)	Foam height, $t = 0$ $t = 5$ (0.1%, mm, 50°C)	Foam height, $t = 0$ $t = 5$ (1.0%, mm, 50°C)	Surface tension (0.1%, dynes/cm)
EP 9-36[a]	97,—,—	14, 0	—	—	—	37.3
EP 38-44	263, 18, 3	34, 24	124, 35	69, 27	135, 44	37.4
EP 40-51	42, 3, 0	62, 48	186, 171	25, 18	64, 32	33.1
EP 50-51	57, 4, 0	66, 23	194, 184	50, 35	98, 40	33.3
EP 78-51	218, 30, 10	82, 69	208, 201	67, 56	110, 91	35.7
EP 18-30	>360, 142, 22	28, 6	19, 0	25, 8[b]	106, 12[b]	41.4

[a] Clear solution at 0.1%, cloudy at 0.5 and 1.0%.
[b] Run at a temperature above cloud point.

TABLE 6
Interfacial Performance Data for High-Molecular Weight POP/POE Block Copolymer Surfactants[a]

Copolymer surfactant	CMC (mg/L)	CMC (molar)	Surface excess (moles/cm^2, E-10)	Area per molecule (Å^2)	ΔG°_{MIC} (kJ/mole)	pC_{20}	CMC/C_{20}	Maximum surface pressure (dynes/cm)
EP 9-36	1,650	6.7 E-4	0.54	309	−28.0	6.4	1,633	35
EP 38-44	329	7.8 E-5	0.64	260	−33.4	6.5	260	35
EP 40-51	207	4.4 E-5	0.81	205	−34.8	6.6	161	39
EP 50-51	311	6.0 E-5	0.79	210	−34.0	6.6	236	39
EP 78-51	605	9.4 E-5	0.59	280	−32.9	6.6	386	36
EP 18-30	359	1.4 E-4	0.57	294	−31.9	6.3	288	31

[a] See Table 3 for abbreviations.

TABLE 7
Cloud-Point Behavior of High-Molecular Weight POP/POE Block Copolymers

Copolymer surfactant	Cloud point, initial (°C)	Cloud point, final (°C)
EP 9-36	20	21
EP 38-44	51	68
EP 40-51	45	76
EP 50-51	55	79
EP 78-51	78	88
EP 18-30	27	31

three copolymers with 51 moles of PO in the hydrophobe. These values were 1–2 dynes/cm higher compared to POB/POE copolymers discussed earlier. These results show that POP/POE copolymers can be effective in lowering surface tension if the hydrophobe is of sufficient length.

Interfacial properties of high–molecular weight POP/POE triblock diols. Table 6 presents a summary of the interfacial properties of the high-molecular weight POP/POE copolymers. A breakdown of each of the properties and comparisons to commercial POB/POE copolymers follows.

CMC values and free energy of micellization. As seen in Table 6, the molar- and weight-basis CMC values are, on the whole, higher than POB/POE values. Free energy of micellization is overall more positive.

Surface-excess concentration and APM at the interface. Surface excess concentrations for high-molecular weight POP/POE block copolymers are listed in Table 6. This is better visualized by discussing the APM at the interface. One might expect that the APM would increase in some proportion with an increase in molecular weight of the copolymer. Results showed, however, that APM values for this set of copolymers were similar to those of lower-molecular weight triblock POP/POE materials (see Table 3) with values in the 200 to 300 Å range. Moreover, APM values are lower overall for the higher–molecular weight series POP/POE triblock diols. This could be a result of chain folding of the POP hydrophobe at the interface. Such a claim would need to be studied by other techniques.

Efficiency and effectiveness of high-molecular weight POP/POE diols. Table 6 shows that pC_{20} values are 0.3–0.7 units higher compared to POB/POE copolymers (see Table 3), indicating more efficient formation of a saturated interface. Effectiveness, or Π_{CMC}, (see Table 6) is similar when compared to POB/POE diols listed in Table 3.

CMC/C_{20} ratio. The CMC/C_{20} ratio can be used to describe how the structural change of increasing the percentage of EO affects absorption and micellization in three homologous copolymers, listed in Table 6. EP 40-51, EP 50-51, and EP 78-51 have a central 3,000 Mw hydrophobe with 40, 50, and 78 moles of EO, respectively. These three lots have the same pC_{20} effectiveness value. The CMC, however, increases as a function of EO content. Using reasoning mentioned earlier, this means that micellization is inhibited when EO content is increased.

Cloud point. Cloud-point data for high-molecular weight POP/POE diols are given in Table 7. Initial cloud points are somewhat proportional to wt% EO in the copolymers.

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