

Surface Properties of Graft Copolymers Surfactants: Behavior at the Water/Toluene Interface

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SYNOPSIS

Poly(propylene oxide-*b*-ethylene oxide) (PPOPEO) surfactant has been used as a surface tension modifier. In this study, the graft copolymer made of poly(methyl methacrylate) (PMMA) main chain and PPOPEO graft chain behavior at water/toluene interface was observed. Interfacial tension measurements were conducted by dissolving the graft copolymer in toluene at a concentration range 1 wt % – 0.0003. The results confirmed the surfactant behavior of graft copolymers, which presented a PMMA/PPOPEO ratio dependence. The critical micellar concentration (CMC) was observed. Above the CMC, the graft copolymers tend to form a monomolecular association that depends upon copolymer molecular weight.

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INTRODUCTION

The most important development in the nonionic surfactants field was the discovery that a gradual variation of hydrophobicity could be obtained by using poly(ethylene oxide) (EO) and poly(propylene oxide) (PO) block copolymers.¹

The surface tension of an aqueous solution increases while the EO/PO ratio is increased, at the same solution concentration, and the reduction of the surface tension depends upon the copolymer structure (triblock, alternated block, star block).²

The surfactant adsorption at the interface reduces the free energy of the system.³⁻⁶ The surfactant mass adsorbed at the liquid-liquid interface can be calculated through the interfacial tension vs. concentration plot by using Gibbs adsorption isotherm [eq. (1)]:

$$\Gamma = - \frac{1}{RT} \frac{\partial \gamma}{\partial \ln C_2} T \quad (1)$$

where Γ is the solute surface concentration (adsorption), γ is the surface (or interface) tension, C is the solution concentration, T is the experimental

temperature, and R is gas constant. Equation (1) means that when the solute concentration is increased and the solution surface tension decreases ($\Gamma > 0$) the solute is adsorbed at the interface. Solute molecules are attracted from the solution bulk toward the surface because solvent molecule interactions are higher than solute-solvent molecules. Accumulation of the solute molecules at the interface decreases the intermolecular interactions at the surface layer.⁷

At high solute concentration at the surface (closest packing), it was observed that the surface area per molecule approaches the limit of $\sim 0.20 \text{ nm}^2$ for all normal fatty acids (C_{14} - C_{18}). It indicates that the molecules are perpendicularly oriented at the interface.⁸

Recent studies about solution behavior of amphiphilic graft copolymers in selective solvents have shown that macromolecular association depends mainly upon the thermodynamic quality of the solvent regarding main and graft chains and the graft chain content.⁹⁻¹²

EXPERIMENTAL

The graft copolymers used in this study were synthesized by macromonomer technique upon free-radical initiation.¹³ The characterization dates are summarized in Table I.

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Table I Characterization of Graft Copolymers

Polymer	Graft Chain	Graft Chain ^a (wt %)	$M_n^b \times 10^{-3}$
PMMA	—	—	14.3
C1	BuPEOPPO	12	43.7
C3	BuPEOPPO	18	80.8
C4	BuPPOPEO	11	78.4
C6	BuPPOPEO	20	67.3
C8	PEOPPOPEO	51	—

^a Determined by ¹H nuclear magnetic resonance (NMR) spectroscopy (Varian VXR-300).

^b Determined by vapor pressure osmometry (VPO) (Wescan 232-A) in toluene at 25°C.

The block copolymers of ethylene oxide and propylene oxide that make up the graft chain were obtained from Grupo Ultra-Divisao Quimica (Maua, S.P., Brazil) (Table II).

The surface tension measurements were performed on a Kruss (Hamburg, Germany) K-10 digital tensiometer at the water/toluene interface, where the graft copolymer was dissolved in toluene. For each copolymer, a surface tension vs. concentration plot was built at the range of 1–0.0003 wt %. The Gibbs adsorption isotherm was used for data treatment.

RESULTS AND DISCUSSION

Surface tension vs. concentration plots provide information about the interface behavior. In general,

these plots present a discontinuity in slope. The first portion of the curve (at lower concentration) is related to the adsorption at the interface governed by the Gibbs adsorption isotherm. The extension of both portions leads to the discontinuity average, which is related to the substance association state in solution. In general, the second portion of the curve (at higher concentration) is a parallel straight line to the concentration axis and indicates that in this step adsorption does not take place.

Nonionic surfactants present a discontinuity in slope at very low concentrations: about 10^{-4} mol/L. Low-molecular-weight poly(ethylene oxide-*b*-propylene oxide) (PEOPPO) macromolecules do not result in significant solution association.¹⁴⁻¹⁶

Figure 1 shows interfacial tension vs. concentration curves of block copolymers (BuPEOPPO,

Table II Characterization of PPOPEO Block Copolymer

Polymer	M_n^a	M_w/M_n^b	OH Index	Monomer Repeat Units ^c	
				EO	PO
BuPPOPEO	900 ± 15	1.23	1.03	6	10
BuPEOPPO	920 ± 15	1.28	1.06	4	11
PEOPPOPEO	1460 ± 25	1.44	2.08	4	22

^a Determined by VPO in toluene at 25°C.

^b Determined by gel permeation chromatography in tetrahydrofuran at 25°C.

^c Determined by ¹H NMR spectroscopy.

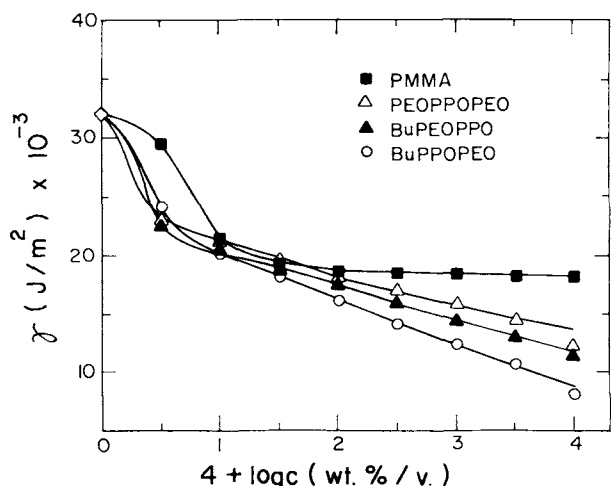


Figure 1 Concentration dependence of the interfacial tension γ of block copolymers (BuPEOPPO, BuPPOPEO, and PEOPPOPEO) and PMMA at 25°C.

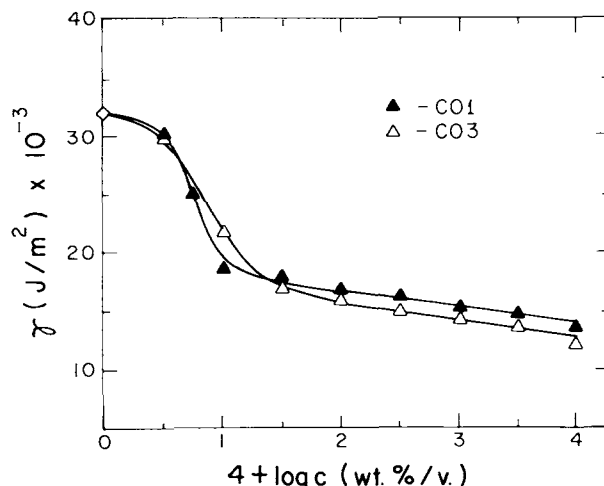


Figure 2 Concentration dependence of the interfacial tension γ of C_1 and C_3 graft copolymers (graft chain: BuPEOPPO) at 25°C.

BuPPOPEO, and PEOPPOPEO) and poly(methyl methacrylate) (PMMA). Ethylene oxide and propylene oxide block copolymers are surface active, reducing the water/toluene interface tension from $32.0 \times 10^{-3} \text{ J/m}^2$ to $\sim 8.0 \times 10^{-3} \text{ J/m}^2$ according to the literature. The system that contains BuPPOPEO macromolecules presents the lowest value to the surface tension, $8.1 \times 10^{-3} \text{ J/m}^2$ (Table III), due to the highest EO/PO ratio. PMMA does not provide a low surface tension yet is able to adsorb at the interface, likely due to pendant ester groups ($-\text{COO}-$).

Figures 2 and 3 show that graft copolymers used in this work present the main and graft chain characteristics. The graft copolymer adsorption at the interface is $\sim 3 \times 10^{-6} \text{ mol/m}^2$ calculated through the first portion of the curve. This result is com-

parable to PMMA. The second portion of the curve leads to low surface tension values like PEOPPO surfactants. The discontinuity in slope is consistent with the association to form micelles of these graft copolymers in solution, and the low slope of the second portion of the curve indicates that this association occurs before surface saturation.

Adsorption and area per group adsorbed results of graft polymers are shown in Table IV. The reduction of solution interface tension (at 1% wt/vol) is indirectly proportional to graft chain content. The

Table III Interfacial Tension of EO/PO Block Copolymers and PMMA Solution in Toluene at 1% (wt/vol)

Polymer	Monomer Repeat Units		Interfacial Tension (J/m^2) $\times 10^3$
	PO	EO	
BuPPOPEO	10	6	8.1
BuPEOPPO	11	4	11.5
PEOPPOPEO	22	4	12.1
PMMA	—	—	18.2

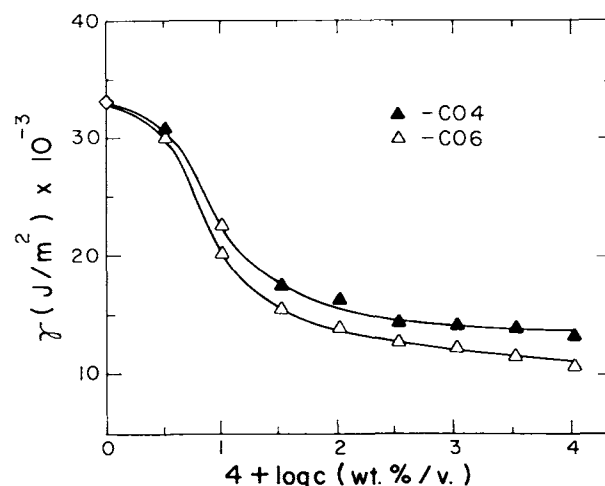


Figure 3 Concentration dependence of the interfacial tension γ of C_4 and C_6 graft copolymers (graft chain: BuPPOPEO) at 25°C.

Table IV Adsorption and Area Per Group Adsorbed

Polymer	Graft Chain (wt %)	1st Slope		2nd Slope		Interfacial Tension ($\text{J/m}^2 \times 10^3$)	Assoc. Point (% wt/vol)
		Γ_1 ($\text{mol/m}^2 \times 10^6$)	Area A_1 (nm^2)	Γ_2 ($\text{mol/m}^2 \times 10^6$)	Area A_2 (nm^2)		
PMMA	—	2.86	0.58	0.00	—	18.2	—
BuPEOPPO	—	—	—	0.56	2.98	11.5	—
C1	12	4.14	0.40	0.28	5.97	13.6	0.0009
C3	18	2.77	0.60	0.29	5.69	12.1	0.0019
BuPPOPEO	—	—	—	0.69	2.39	8.1	—
C4	11	2.88	0.58	0.30	5.46	13.4	0.0020
C6	20	3.47	0.48	0.26	6.32	10.6	0.0017
PEOPPOPEO	—	—	—	0.53	3.16	12.1	—
C8	51	2.39	0.69	0.65	2.56	8.4	0.0026

Results obtained by using Gibbs adsorption isotherm.

C8 graft copolymer (5 wt % PEOPPOPEO) leads to lower interface tension ($8.4 \times 10^{-3} \text{ J/m}^2$) than PEOPPOPEO block copolymer in solution ($12.1 \times 10^{-3} \text{ J/m}^2$). The adsorption does not vary in the same way as tension: It depends upon the molecule structure. In the copolymers in which the graft chains are made up of BuPPOPEO; higher graft chain content provides more adsorption. In this case, it should also be taken as the highest EO/PO ratio of the graft chain (Table III). The copolymers in which the graft chains are made up of BuPEOPPO behave in the opposite way.

Two kinds of behaviors can be suggested for the last two cases by regarding the area occupied per molecule as follows:

1. *Adsorption \propto 1/% graft chain in copolymer.* Besides graft chain adsorption, main chain

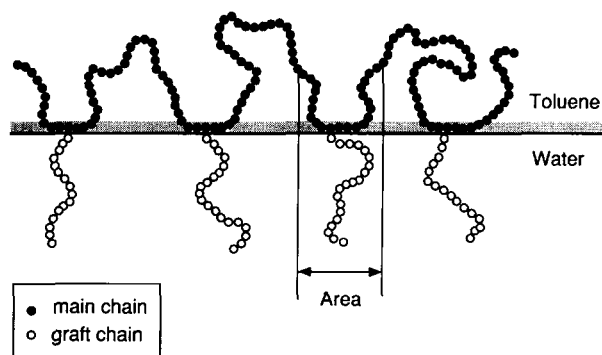


Figure 4 Schematic representation of graft copolymer at the water/toluene interface. The area calculated concerns each graft chain adsorbed.

adsorption is also proposed so that when the copolymer has more graft chains the main chain segments between two graft chains become shorter, making it easier for ester group interaction at the interface; then, the molecule occupies a bigger area.

2. *Adsorption \propto % graft chain in copolymer.* The higher the graft chain content, the easier for packing at the interface, thus obstructing the main chain interaction at the interface; then, the molecule occupies a smaller area, i.e., adsorption increases.

Gibbs adsorption isotherm provides values about the area that one molecule occupies at the interface. The adsorption is given in molecules/area; therefore, the inverse is given in area/molecule. However, the area/molecule values obtained by the graft copolymers ($A_1 \approx 0.5 \text{ nm}^2$) are similar to area/molecule values of low-molecular-weight substances, for instance, isostearic acid (area = 0.32 nm^2) and tri-*p*-cresil phosphate (area = 0.95 nm^2).⁸ These results indicate that when measurement is done with these graft copolymers the values correspond to each graft adsorbed at the interface and the main chain becomes a branch from this point of view (Fig. 4).

The calculated area per molecule adsorbed values found above the association point (A_2) concerns the area per aggregate. In the determination of the number of molecules (graft copolymers) that make up the aggregate, the average number of graft chains in the copolymer molecule should be considered. The results summarized in Table V show that in this system the graft copolymers tend to monomolecu-

Table V Association Molecule Numbers

Polymer	M_n Graft Copolymer $\times 10^{-3}$	M_n Graft Chain	X^a	Graft Chain Per Molecule (average)	A_2/A_1^b	Assoc. Number of Molecules ^c
C1	43.7	920	69	6	14.87	2.5
C3	80.8	920	42	16	9.48	0.5
C4	78.4	900	66	10	9.48	1.0
C6	67.3	900	35	15	13.20	1.0

^a X = average number of methyl methacrylate units between two graft chains.

^b Area obtained (1) below and (2) above the association point.

^c Approximate values.

larly associate. Further, the number of molecules that make up the aggregates depends upon the molecular weight of the graft copolymer.

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