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Maryjo Doiron<sup>a</sup>; Jonathan Moulins<sup>a</sup>; Rebecca Dean<sup>a</sup>; Rama M. Palepu<sup>a</sup>

<sup>a</sup> Department of Chemistry, St. Francis Xavier University, Canada

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## Interactions of alkyl triphenyl phosphonium bromides with aqueous solutions of LM200 and JR400 polymers

MARYJO DOIRON, JONATHAN MOULINS, REBECCA DEAN and RAMA M. PALEPU\*

Department of Chemistry, St. Francis Xavier University,  
Antigonish, NSB2G 2W5, Canada

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The interactions of the cationic cellulose ether derivatives JR400 and the hydrophobically modified derivative LM200 with cationic alkyl triphenylphosphonium bromides, were investigated in aqueous media. Conductometric, tensiometric and fluorescence techniques were employed in this study. The presence of polymer induced surfactant aggregation and polymer bound aggregates, were detected for C<sub>16</sub> and C<sub>14</sub> triphenylphosphonium bromide surfactants with LM200. Gibbs free energy of transfer and the dielectric constant values sensed by the fluorescent probe at the micellar interface were evaluated and discussed in terms of strength of interaction between the polymers and surfactants.

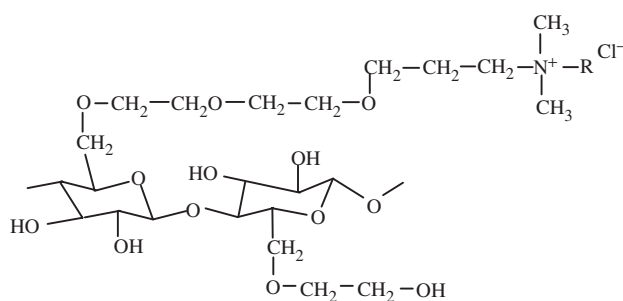
*Keywords:* Cationic surfactants; Hydrophobically modified cationic hydroxycellulose ether; Conductivity

### 1. Introduction

Polymer-surfactant interaction studies have gained growing interest in the past few decades due to their relevance in many industrial applications [1–6]. Polymer-surfactant solutions are employed in tertiary oil recovery to effectively dislodge the trapped oil [7,8]. The polymer-surfactant gels are suitable for use, as templates for the synthesis of nanomaterials [9,10]. These systems have also found applications in cosmetic formulation, as a thickening agent, coatings and in pharmaceutical products [3]. The majority of the systems investigated involve nonionic polymers with anionic surfactants and polyelectrolytes with oppositely charged surfactants. It is well-known that the anionic surfactants interact favourably with nonionic polymers, whereas cationic surfactant interact weakly or moderately with nonionic polymers depending on the specific conditions [11,12]. In recent years, hydrophobically modified water soluble polymers have been used in such studies [13–19]. Surfactant-biopolymer interaction studies are of relevance to biotechnology [20,21] and the interaction of cationic surfactants with DNA for favourable transfer of genes in living cells have been

\*Corresponding author. Tel.: +902 867 3886. Fax: +902 867 2414. Email: rpalepu@stfx.ca

reported [22,23]. The interaction between polymer and surfactant takes place at a particular concentration known as the critical aggregation concentration (cac) and usually occurs at a concentration lower than the critical micelle concentration (cmc). It is believed that initially the surfactant binds to the polymer backbone and once the polymer is saturated, the excess of surfactant molecules form free micelles and polymer bound aggregates coexists with free micelles. The cac values can be several orders of magnitude below the cmc values. Recent calorimetric and electrical birefringence studies have revealed that polymer/surfactant association occurs below cac and it is non-cooperative below cac [24,25]. Langevin and co-workers have shown that the cac is not affected by the polymer charge density (in the case of ionic polymers) and depends on polymer concentration [26]. In hydrophobically modified polymers, the presence of hydrophobic segment may result in a tendency of the polymer to form hydrophobic aggregates and also provide the unique ability to form associations with surfactants of the same charge [13]. This phenomenon is lacking in traditional polyion-surfactant systems of like charge [27]. In the present study, we report the results of binding of alkyl triphenyl phosphonium bromides (ATPPB) of varying alkyl chain lengths ( $C_{16}$ – $C_{10}$ ) with Quatrisoft<sup>®</sup> LM200 and JR400 water soluble polymers (scheme 1). The systems were investigated using conductometric, flurometric and tensiometric methods to obtain information on the nature of the interaction the surfactant undergo with the polymers. Conductometric measurements were performed to determine the cac, cmc and the degree of counter ion dissociation of the polymer-surfactant complex. Tensiometric measurements were performed to support the data obtained from conductometric method. Fluorescence measurements were performed to obtain the cmc, cac values and information on the micropolarity sensed by the probe at the micellar interface. Pyrene 1-carboxylaldehyde (PCA), crystal violet (CV) and pyrene (Py) were used as fluorescent probes in the present investigation. Both PCA and Py are nonionic and sensitive to the polarity of the medium. The nonionic probes are solubilised at the micellar interface [28,29], thereby sensing the micropolarity at the interface. The emission spectra of PCA is red shifted with an increase in polarity of the media and found to vary linearly with the dielectric constant of the media between ( $\epsilon = 10$ – $80$ ). Thus from the fluorescence maximum of the probe solubilised in the micelle, the dielectric constant of the micellar interface can be determined. In the case of



JR400 R = CH<sub>3</sub>  
LM200 R = C<sub>12</sub>H<sub>25</sub>

Scheme 1. Structural unit formula of JR400 and LM200.

pyrene, the ratio of the relative intensities of the (0,0) and (0,3) band decreases with a decrease in the polarity sensed by the probe [29]. The fluorescence emissions of CV are dependant on the microviscosity of the media [30] and the change in the microviscosities sensed by the probe can be used to determine cac and cmc values in the present study.

## 2. Experimental

The cationic cellulose ether derivatives JR400 and LM200 were gift samples from Amerchol (USA) and were used without further purification. The average molar masses were approximately 400,000 and 100,000 Da. The degree of substitution was found to be  $2.0 \times 10^{-4}$  mole of hydrophobic chains per a gram of polymer for LM200 and this corresponds to approximately 3.4% by weight or one substitution per every 19 glucose units [31]. Alkyl triphenylphosphonium bromides were the same samples that were used in our previous investigations [32,33]. All the surfactants were recrystallised from acetone and exhibited no minimum in their surface tension *versus* concentration plots. Fluorescence probes were the same as the ones used in our previous investigations [34].

### 2.1. Methods

Conductivity measurements, were performed using an automatic conductivity bridge (Radiometer, Copenhagen) operating at 1000 Hz with a dip cell having a cell constant  $1.03 \text{ cm}^{-1}$ . The specific conductivity at 298 K was measured as a function of surfactant concentration and the values of cac and cmc were obtained from the break points of the plots of conductivity *versus* concentration of the surfactant. The polymer stock solutions were prepared 24 h prior to use. All polymer-surfactant solutions were prepared using stock polymer solution and sonicated to ensure homogeneity.

Fluorescence measurements were carried out using a JY Hariba Spex Fluoromax-3 fluorimeter using a 1 cm quartz cuvette. For the pyrene fluorescence experiments, the pyrene concentration was kept at  $1.0 \times 10^{-6} \text{ M}$  in all solutions and the emission spectrum of pyrene was measured as a function of varying surfactant constant. The fluorophore was excited at a wavelength 340 nm. The excitation and emission slit widths were at 1.5 and 2.0 nm wide, respectively. For the fluorescence spectrum of CV, the probe was excited at 590 nm and the emission range of 600–700 nm was scanned. The slit widths for excitation and emission were 7.00 and 9.00 nm, respectively. The dye concentration was maintained at  $1.0 \times 10^{-5} \text{ M}$  in all solutions investigated. The probe concentration of PCA was kept at  $9.0 \times 10^{-7} \text{ M}$  and excitation wavelength was 370 nm and the slit widths for both excitation and emission were maintained at 5 nm. Surface tension measurements of polymer-surfactant mixtures at 298 K were obtained with a Fisher surface tensiometer 21 as described previously [35].

## 3. Results and discussion

Figure 1 is a representative plot of specific conductivities of C<sub>14</sub> and C<sub>16</sub> TPPB in aqueous solution of LM200. The deviation from linearity in the conductivity plots in

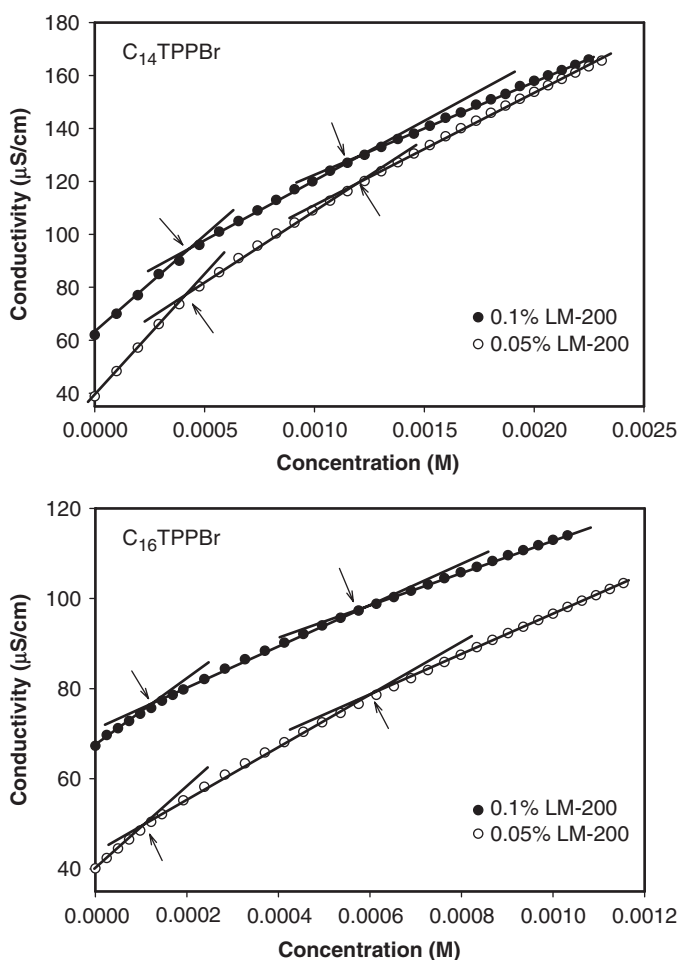


Figure 1. Conductometric titrations of  $C_{14}$  and  $C_{16}$  TPPB with aqueous solutions of LM200.

the pre cmc or near cmc region is indicative of the presence of association of surfactant with polymer cac. The shift in the cmc to higher values also suggests, the existence of polymer-surfactant association. Only one break was exhibited for  $C_{12}$  and  $C_{10}$  surfactants with LM200 and all alkyl TPPB with JR 400 (figure 2) at a slightly higher concentration than the reported cmc values in aqueous solutions. The cmc and cac values are presented in tables 1 and 2 for LM200 and JR400, respectively.

The degree of counter ion dissociation ( $\alpha_{cac}$ ) was obtained from the ratio of slopes of pre cac ( $S_1$ ) and pre cmc ( $S_2$ ) and the values for  $\alpha_{cmc}$ , were obtained from the ratio of slopes of post cmc ( $S_3$ ) and ( $S_1$ ). The alpha values obtained are also included in tables 1 and 2.

Figure 3 depicts the variation of surface tension of  $C_{14}$  and  $C_{16}$  TPPB in LM200 solution. The cac and cmc values are determined from the break points in the surface tension plots and the values are also listed in table 1. The values obtained from surface tension measurements are in fair agreement with the values obtained from conductivity measurements. In case of  $C_{12}$  and  $C_{10}$  surfactants in LM200 and for all in JR400,

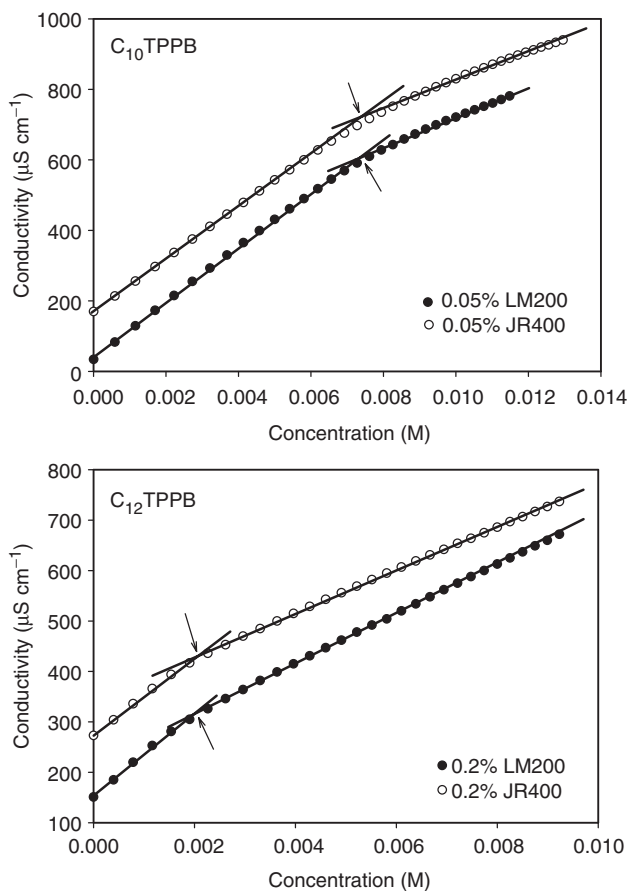


Figure 2. Conductometric determination of cmc of  $C_{12}$  and  $C_{10}$  TPPB in aqueous solution JR400 and LM200.

Table 1.  $c_{ac}$ , cmc and counter ion dissociation of ATPBB in aqueous LM200 solutions.

Surfactant	Polymer mass (%)	$c_{ac}^{\#}$	$\alpha_{cac}$	$cmc^{a\#}$	$\alpha_{cmc}$	$c_{ac}^{b\#}$	$cmc^{b\#}$	$\Delta G_t^*$
$C_{16}$ TPPB	0.05	$1.53 \times 10^{-4}$	0.65	$5.15 \times 10^{-4}$	0.45	$1.56 \times 10^{-4}$	$5.5 \times 10^{-4}$	-1.68
	0.10	$7.54 \times 10^{-5}$	0.70	$5.02 \times 10^{-4}$	0.44	$9.36 \times 10^{-5}$	$6.1 \times 10^{-4}$	-1.30
$C_{14}$ TPPB	0.05	$4.86 \times 10^{-4}$	0.66	$1.38 \times 10^{-3}$	0.47	$4.1 \times 10^{-4}$	$7.5 \times 10^{-4}$	-1.53
	0.10	$4.51 \times 10^{-4}$	0.64	$1.45 \times 10^{-3}$	0.45	$3.1 \times 10^{-4}$	$9.4 \times 10^{-4}$	-0.45
	0.20	$4.09 \times 10^{-4}$	0.65	$1.47 \times 10^{-3}$	0.47	$3.0 \times 10^{-4}$	$1.0 \times 10^{-3}$	-0.17
$C_{12}$ TPPB	0.05			$1.73 \times 10^{-3}$	0.45			
	0.10			$2.09 \times 10^{-3}$	0.53			
	0.20			$2.40 \times 10^{-3}$	0.53			
$C_{10}$ TPPB	0.05			$7.15 \times 10^{-3}$	0.51			
	0.10			$7.40 \times 10^{-3}$	0.49			
	0.20			$8.20 \times 10^{-3}$	0.49			

<sup>a</sup>conductometric method.

<sup>b</sup>tensiometry.

\*kJ per mole (error 5%).

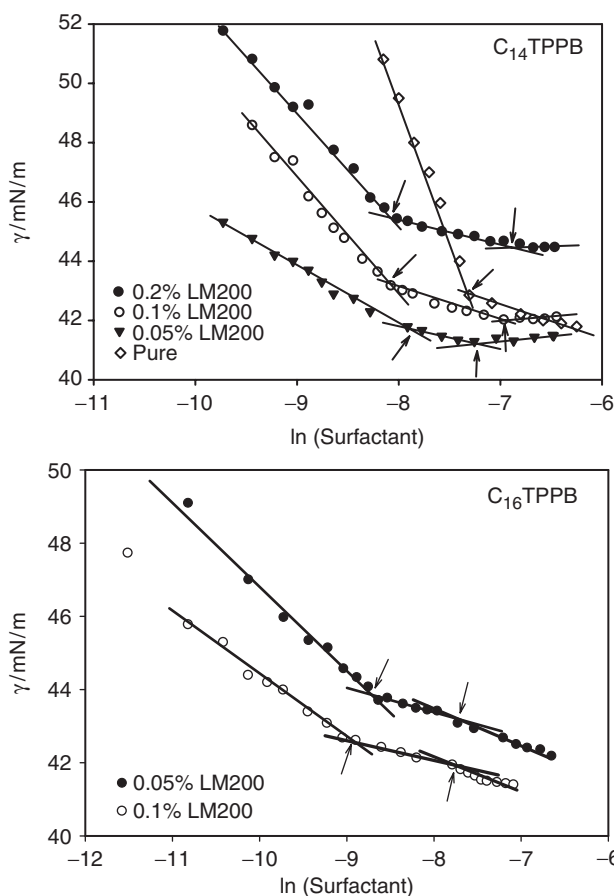
<sup>#</sup>units: mol/L.

Table 2. cmc values of ATPPB in aqueous JR400 solutions.

Surfactant	Polymer (mass%)	cmc <sup>a, #</sup>	$\alpha_{cmc}$	cmc <sup>b #</sup>
C <sub>16</sub> TPPB	0.05	$2.32 \times 10^{-4}$	0.64	
	0.20	$2.83 \times 10^{-4}$	0.63	$2.0 \times 10^{-4}$
C <sub>14</sub> TPPB	0.05	$6.28 \times 10^{-4}$	0.56	
	0.20	$6.40 \times 10^{-4}$	0.46	$6.4 \times 10^{-4}$
C <sub>12</sub> TPPB	0.05	$2.15 \times 10^{-3}$	0.60	
	0.20	$2.25 \times 10^{-3}$	(0.58)	$2.4 \times 10^{-4}$
C <sub>10</sub> TPPB	0.05	$7.29 \times 10^{-3}$	(0.49)	
	0.20	$7.96 \times 10^{-3}$	(0.45)	$1.0 \times 10^{-3}$

<sup>a</sup>conductometric method.

<sup>b</sup>fluorometric method.

<sup>#</sup>units moles per litre.

 Figure 3. Tensiometric plots of C<sub>14</sub> and C<sub>16</sub> TPPB in LM200 solutions.

the plots exhibited only one break at cmc (plots not shown). Apparent lack of a break for cac in both conductivity and surface tension plots for these systems suggests that the interaction between the polymers and surfactants was not as strong as in the case of C<sub>16</sub> and C<sub>14</sub> surfactants with LM200.

An increase in cmc values and a decrease in cac, were observed with an increase in LM200 concentration. Also, the degrees of counter ion dissociation ( $\alpha_{\text{cmc}}$ ) are found to be lower than ( $\alpha_{\text{cac}}$ ) indicating stabilisation of the micelles in the presence of polymer. The stability and the strength of interaction between the surfactants are the polymer LM200 can further be evaluated by calculating the decrease in Gibbs free energy of micellisation employing charged pseudo phase separation model [36]. It is given by the following equation.

$$\Delta G_i^{\circ} = RT[(2 - \alpha_{\text{cmc}}) \ln X_{\text{cmc}} - (2 - \alpha_{\text{cac}}) \ln X_{\text{cac}}] \quad (1)$$

where  $X_{\text{cmc}}$  and  $X_{\text{cac}}$  are the values of cmc and cac expressed on the mole fraction scale. The reduction in free energy of micellisation in the presence of LM200 is negative and small in magnitude indicating weaker interaction between the polymer and surfactant as well as stabilisation of micelles in the presence of LM200.

### 3.1. Fluorescence spectroscopy

The polymer/surfactant interactions, were further investigated in detail employing PCA as a probe. Plots of  $\lambda_{\text{max}}$  versus surfactant concentration are presented in figures 4 and 5 for LM200 and JR400, respectively. Only  $C_{16}$  and  $C_{14}$  TPPB with LM200 exhibited break points for both cac and cmc (figure 4). For the rest of surfactants, only one break for cmc is observed (figures 4 and 5). The values of cmc and cac are presented in table 3. Proton NMR studies have shown that the aromatic aldehydes, such as PCA is stabilised with hydrophobic moiety in the micellar core and with hydrophobic group protruding into the micelle and the hydrophilic part anchored at the micellar interface. The dielectric constant ( $\epsilon$ ), sensed by the probe corresponding to  $\lambda_{\text{max}}$  is obtained from the linear plot  $\lambda_{\text{max}}$  versus  $\epsilon$  [28]. The values are reported in table 3. The dielectric constant sensed by the probe varied in the range of 21–29 for the systems investigated. The interaction of  $C_{14}$  TPPB with LM200 is further investigated with both CV and Py as probes (figure 6) and the results were included in table 3 and they are in fair agreement with the results obtained employing PCA.

## 4. Conclusions

The results indicate that the hydrophobically modified polymer (LM200) interacts with  $C_{16}$  and  $C_{14}$  TPPB to form micelle-like aggregates from the association of the alkyl tails of the monomers with the  $C_{12}$  chains of the LM200 polymer. In addition to the hydrophobically driven interactions, it is also possible that the pi cloud of the head group region of the surfactant may interact favourably with the positive charge on the quaternary nitrogen of the dodecyl groups of LM200. The overall weak interactions are due to a sum of favourable hydrophobic forces and the sum of repulsive forces between the like charges and the steric hindrance associated with bulky head groups.



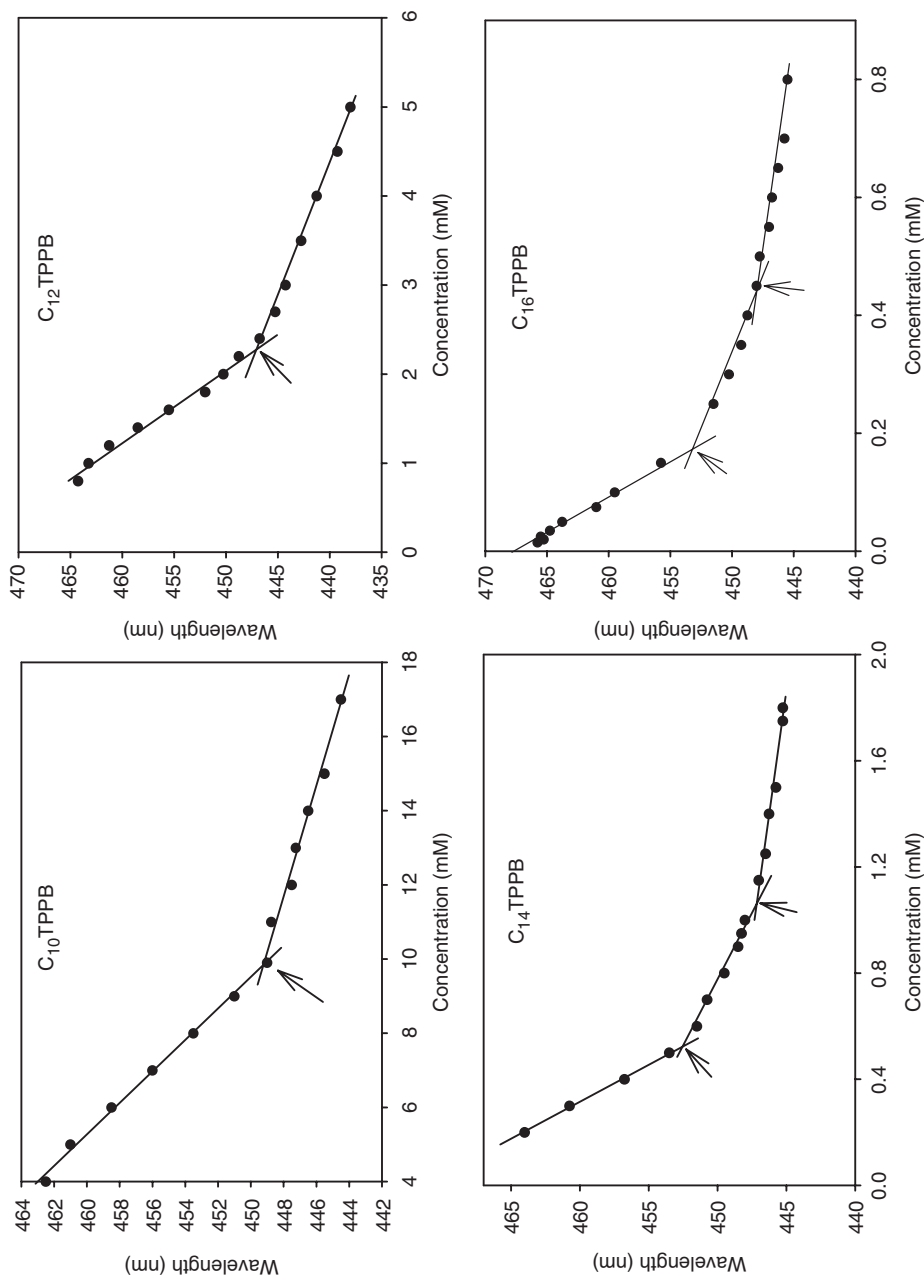


Figure 4. Fluorometric determination of cac and cmc employing PCA as a probe.

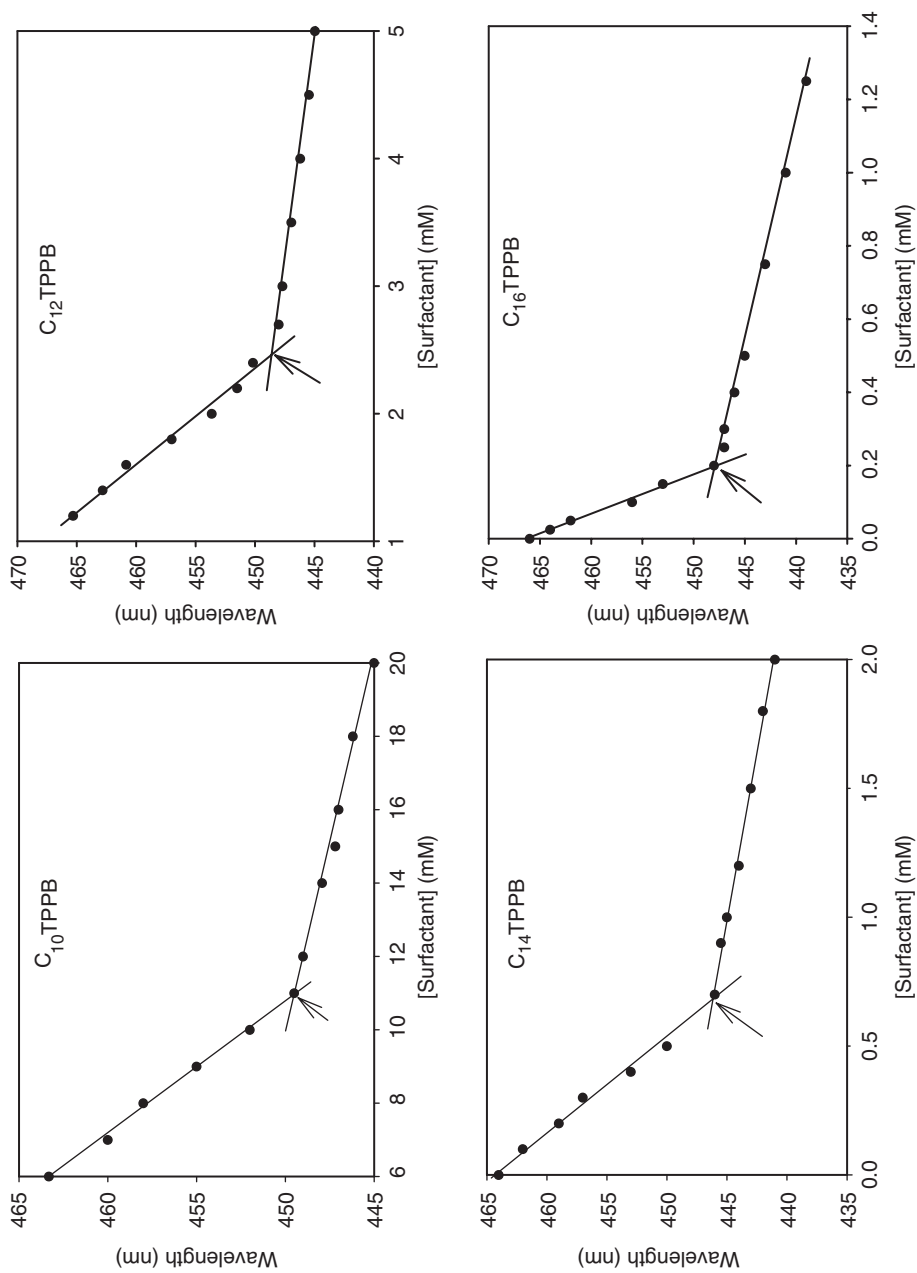


Figure 5. Fluorometric investigations of interactions of alkyl triphenylphosphonium bromides with aqueous solutions of JR-400.

Table 3. Fluorometric determination of  $cac$ ,  $cmc$  and estimates of polarity at micelle-water interface using PCA as probe.

	$cac^{\#}$	$cmc^{\#}$	$\epsilon$ (in $H_2O$ )	$\epsilon$ (in 0.1% LM200 solution)
$C_{16}TPPB$	$1.5 \times 10^{-4}$	$4.6 \times 10^{-4}$	28.7 (0.8 mM)	26.8 (0.8 mM)
$C_{14}TPPB$	$5.0 \times 10^{-4}$	$1.1 \times 10^{-3}$	25.8 (2.0 mM)	24.8 (2.0 mM)
	$4.1 \times 10^{-4a}$	$1.1 \times 10^{-3a}$		
	$3.0 \times 10^{-4b}$	$6.8 \times 10^{-4b}$		
$C_{12}TPPB$	–	$2.2 \times 10^{-3}$	22.9 (5 mM)	21.5 (5 mM)
$C_{10}TPPB$	–	$9.8 \times 10^{-3}$	26.8 (20 mM)	23.9 (20 mM)

<sup>a</sup>crystal violet.

<sup>b</sup>pyrene as fluorescence probes.

<sup>#</sup>units moles<sup>-1</sup>.

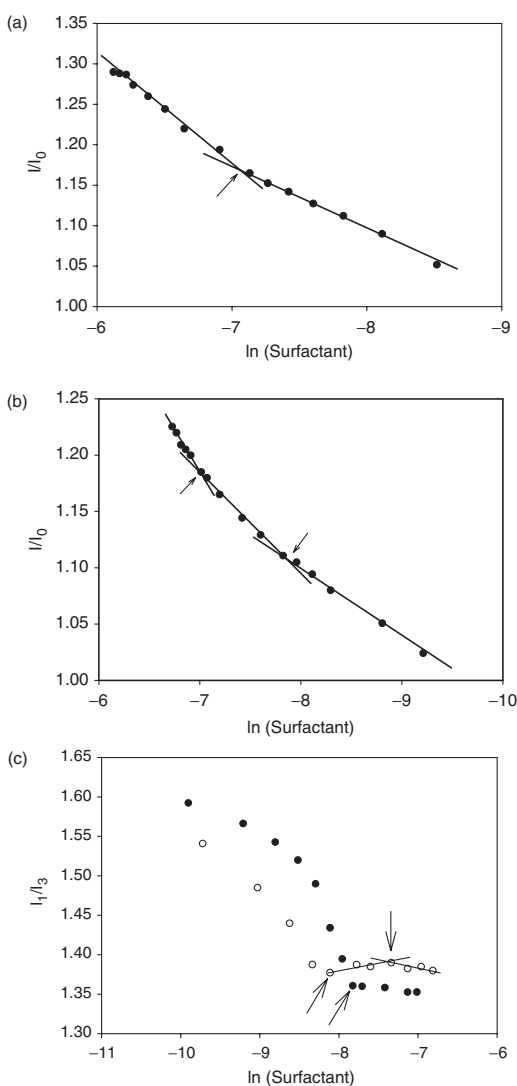


Figure 6. Fluorometric investigations using CV as a probe: (a): In  $H_2O$ , (b): In 0.1% LM200 aqueous solution, (c): Pyrene as a probe dark circles ( $H_2O$ ) and open circles (0.1% aqueous LM200).

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