

# Interaction between Cetyl Pyridinium Chloride and Water-Soluble Polymers in Aqueous Solutions

Inmaculada García-Mateos, Soraya Pérez, and M. Mercedes Velázquez<sup>1</sup>

*Departamento de Química Física, Facultad de Farmacia, Universidad de Salamanca, Apdo. 449, E-37080 Salamanca, Spain*

Received April 18, 1997; accepted August 7, 1997

**The interaction between cetyl pyridinium chloride and different-molecular-weight poly(vinylpyrrolidone) (PVP) and poly(ethylene glycol) (PEG) polymers has been investigated by means of electrical conductivity and fluorescence probing. No interaction between the low-molecular-weight PVP polymers and the surfactant was detected, whereas a significant interaction was observed between high-molecular-weight PVP polymers or PEG polymers and cetyl pyridinium chloride. The results indicate that polymer-surfactant aggregates start to form at a surfactant concentration higher than the critical micelle concentration of micelles without polymers. In contrast, the degree of ionization and the interface polarity decrease as compared with values of micelles without polymers. The Gibbs free energy associated with the interaction was also calculated. The values show that the addition of polymers stabilizes polymer-surfactant aggregates.** © 1997 Academic Press

**Key Words:** cetyl pyridinium chloride; poly(vinylpyrrolidone); poly(ethylene glycol); pyrene 1-carboxaldehyde; polymer-surfactant interaction; electrical conductivity; fluorescence probing.

## INTRODUCTION

The interaction between polymers and surfactants in aqueous solution has attracted much interest in recent years due to the application of these systems in many industrial products such as paints, coatings, cosmetic products, and tertiary oil recovery (1–4). The most extensively studied systems have been those consisting of uncharged polymers and ionic surfactants or polyelectrolytes and oppositely charged surfactants, respectively. In the first category a strong interaction between uncharged polymers such as poly(vinylpyrrolidone) (PVP) (5), poly(vinyl alcohol) (PVA) (6), and poly(ethylene oxide) (PEO) (7) and anionic surfactants like sodium dodecyl sulfate has been observed. Conversely, cationic surfactants interact only weakly, if at all, with PEO or PVP (2), while for more hydrophobic polymers such as poly(propylene oxide) (5), poly(vinylmethyl ether) (8) or hydroxypropyl cellulose (9), significant interactions were detected. In all cases it has been observed that the interaction

takes place when the surfactant concentration is higher than a value termed the critical aggregation concentration (CAC). Then, there is binding of the surfactant onto the polymer in the form of aggregates (1). Once the polymer is saturated with the surfactant, the excess of surfactant molecules forms free micelles and at higher surfactant concentrations polymer-bound aggregates coexist with free micelles.

In polyelectrolyte oppositely charged surfactant systems, the interaction clearly results from strong coulombic forces. In contrast to nonionic polymer systems, the interaction leads to phase separation. This fact limits the studies to surfactant concentrations close to the critical micelle concentration (CMC). The interaction begins at surfactant concentrations below the CMC of the pure surfactant. At high polyelectrolyte concentrations a second, gel-like, liquid phase starts to form and can be separated at surfactant concentrations much lower than those corresponding to charge neutralization. The phase behavior (10) and surfactant aggregation number (11) have been obtained for some surfactant-polyelectrolyte systems.

In systems consisting of uncharged polymers and ionic surfactants the driving forces that lead to complex formation are still poorly understood. Several interpretations have been used to explain the difference between the behavior of cationic and anionic surfactants (12–14). However, there is not a unified theory to interpret this behavior. To propose a general model for polymer-surfactant interaction it is necessary to study the effect of the polymer hydrophobicity or the head group surfactant charge on the interaction in a great variety of systems. In the case of a cationic surfactant these studies are limited by its weak interaction with the uncharged polymers. Therefore, the aim of this work is to study the interaction of the cationic surfactant cetyl pyridinium chloride and different-molecular-weight poly(vinylpyrrolidone) and poly(ethylene glycol) polymers. The current study uses conductivity measurements and fluorescence spectroscopy to examine the polymer-surfactant interaction. Conductivity measurements were performed for the determination of the CMC and the degree of micelle ionization with and without polymers. Fluorescence probing measurements were performed for the determination of CMC values and to obtain

<sup>1</sup> To whom correspondence should be addressed.

information on the polarity of the water-micelle interface. The fluorescent probe was pyrene 1-carboxaldehyde. This probe is solubilized at the micellar interface (15) and its maximum of the emission spectrum is red shifted when the solvent polarity increases. The shift of this maximum is linear with the solvent dielectric constant for values between 10 and 80 (16). Thus, from the position of the fluorescence maximum of the probe solubilized in the micelle, the dielectric constant of the micellar interface can be obtained.

## MATERIALS AND METHODS

### Materials

*N*-Cetyl pyridinium chloride (CPy), from Merck, was used without further purification. The surfactant showed no minimum in the surface tension-concentration plot, confirming its purity. The fluorescent probe pyrene 1-carboxaldehyde (PyCHO), from Aldrich, was recrystallized several times from ethanol.

Poly(vinylpyrrolidone) fractions PVP K15 (MW = 10,000 g/mol), PVP K25 (MW = 24,000 g/mol), PVP K30 (MW = 40,000 g/mol), PVP K90 (MW = 360,000 g/mol), and poly(ethylene glycol) fractions PEG 20000 (MW = 17,000 g/mol) and PEG 35000 (MW = 34,000 g/mol) were used as received from Fluka. The molecular weights were provided by the manufacturer. Aqueous polymer solutions always give a neutral pH.

The solutions were prepared with water obtained after treatment with a Milli-Q system from Millipore.

### Conductivity Measurements

The correct determination of the CMC requires a large number of experimental results, so a technique of conductometric titration was employed. Each curve has between 40 and 50 conductivity/surfactant concentration values. In micellar solutions without polymers the curve contains 120 experimental values. CMC values were taken from the intersection of the tangents drawn before and after the breakpoint in the conductivity-versus-surfactant concentration plot.

The electrical conductivity was measured using a CDM 83 (Radiometer, Copenhagen) conductometer operated at 586 and 4.69 kHz and an Ingold conductivity cell of  $0.974 \pm 0.004 \text{ cm}^{-1}$ . The constant cell was calibrated with solutions of KCl of known concentration (17). All measurements were performed at  $25.0 \pm 0.1^\circ\text{C}$ .

### Fluorescence Measurements

The incorporation of pyrene 1-carboxaldehyde into micelles was carried out as follows: An appropriate volume of solution of pyrene 1-carboxaldehyde of known concentration in methanol was poured into a volumetric flask and the solvent was evaporated by slow passage of  $\text{N}_2$ . The solution of surfactant and mixtures of polymer-surfactant were added to

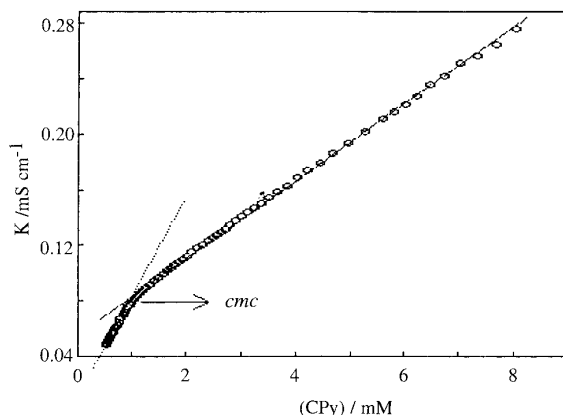


FIG. 1. Conductivity versus cetyl pyridinium chloride concentration for solutions without polymers.

the evaporated residue, and the resulting solution was stirred until the probe was solubilized. The probe concentration was kept at  $0.9 \mu\text{M}$  and was determined by monitoring the absorbance at 370 nm ( $\epsilon = 2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).

The emission spectra were recorded with a Shimadzu RF-540 spectrofluorometer. The excitation wavelength was 370 nm, and both excitation and emission slits were 5 nm.

## RESULTS AND DISCUSSION

### Determination of the Critical Micelle Concentration by Conductivity Measurements

The study of the interaction between CPy and poly(vinylpyrrolidone) and poly(ethylene glycol) polymers was carried out by determining the CMC of micelles in the absence and presence of polymers.

The CMC of a surfactant in water is determined by the appearance of a discontinuity in the variation of some solution properties as a function of surfactant concentration. In some cases a second breakpoint in the solution property appears at a surfactant concentration higher than the CMC of aqueous surfactant. The interpretation provided by most authors is that this second break corresponds to structural micellar changes, as a sphere-to-rod transition.

Recently, a second CMC for CPy (3.4 mM) was reported (18). To confirm this CMC we obtained the electrical conductivity of solutions containing surfactant concentrations in the range 0.4 to 8 mM. The highest surfactant concentration is about nine times the CMC of pure surfactant. Figure 1 shows these results. In view of these results no second break appears in this curve. The presence of only one discontinuity was confirmed by fluorescence probing; results are discussed in the next section.

The CMC of CPy pure surfactant was calculated more accurately by using a range of surfactant concentration of 0.4 to 1.5 mM. The average CMC value from several deter-

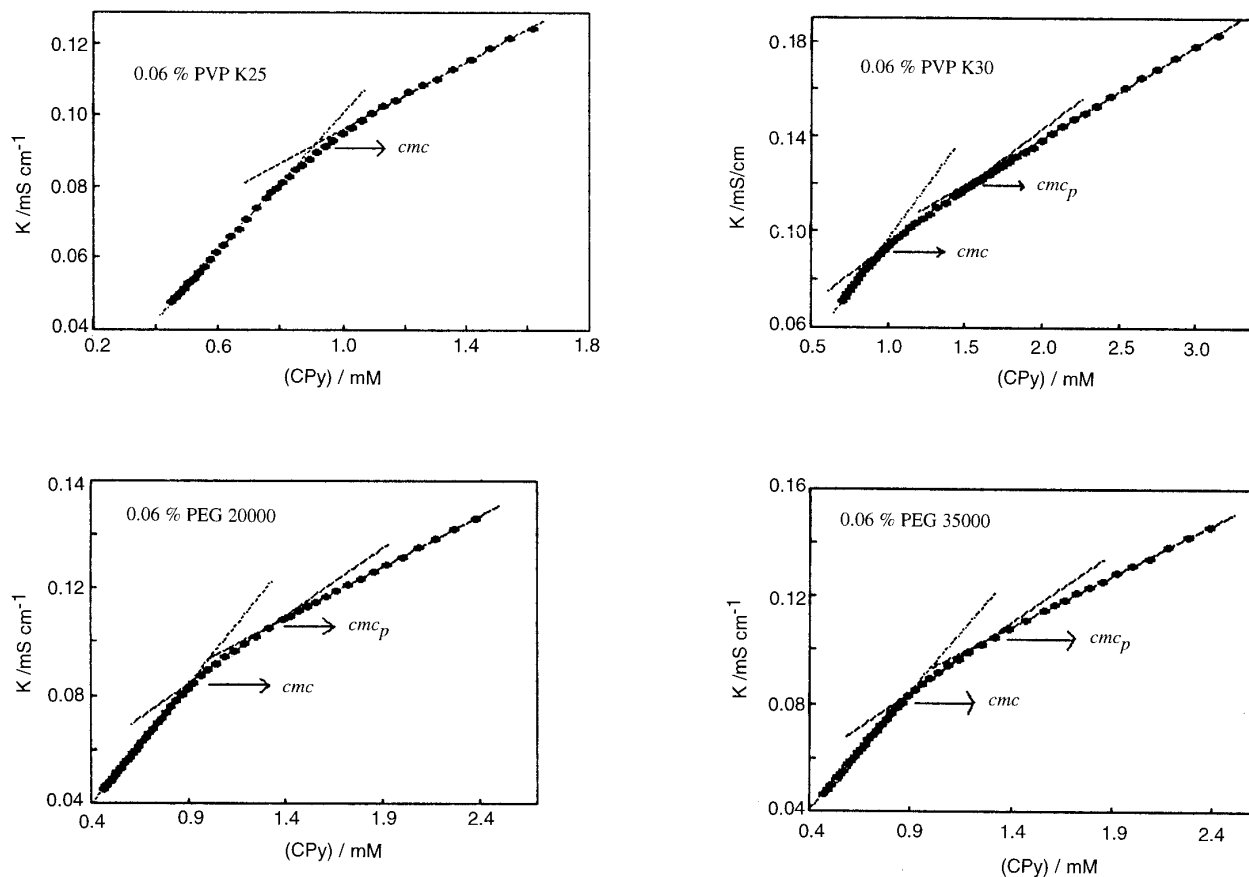


FIG. 2. Conductivity versus cetyl pyridinium chloride concentration for solutions with different polymers.

minations was  $9.1 \pm 0.1 \cdot 10^{-4} M$ . This value agrees with the value found in the literature (19).

The above-mentioned methodology was used to determine CMC values of micellar aggregates containing polymers. To study the effect of the composition on the surfactant-polymer interactions, the polymer content, given as a weight percentage of the polymer to water fraction, has been systematically modified in the range 0.001–0.10%.

The addition of PVP polymers to CPy aqueous solutions induces different behaviors as a function of the polymer molecular weight. When PVP K15 or PVP K25 was added, the trend of variation of the electrical conductivity with the surfactant concentration is similar to that in the absence of polymers; i.e., only a discontinuity in the conductivity/surfactant concentration curves was detected (Fig. 2). The CMC remains constant with the polymer concentration at a value of  $9.18 \pm 0.06 \cdot 10^{-4} M$ . This value agrees with the CMC of the pure surfactant; thus, it can be concluded that there is no interaction between these polymers and cetyl pyridinium chloride. This fact is also observed when low concentrations of PVP K30 ( $<0.02\%$ ) are added to surfactant solutions. At higher PVP K30 concentrations, two breaks in the conductivity curves appear (Fig. 2). The CMC

values obtained from these breakpoints are listed in Table 1. The lowest CMC agrees to that corresponding to aqueous surfactant and is associated with the pure micelle aggregation process. The second CMC ( $CMC_p$ ) appears at higher surfactant concentration and linearly varies with the polymer content.

TABLE 1  
Critical Micelle Concentration and Degree of Micelle Ionization of Aqueous Cetyl Pyridinium Micelles in the Presence of Different Concentrations of PVP K30

% PVP K30	CMC $\times 10^4$ (M)	CMC <sub>p</sub> $\times 10^3$ (M)	$\alpha$	$\alpha_p$
0.005	9.13	—	0.56	—
0.008	9.12	—	0.51	—
0.01	9.07	—	0.53	—
0.015	9.06	—	0.50	—
0.02	8.69	1.15	0.65	0.48
0.03	9.00	1.28	0.54	0.42
0.402	9.10	1.34	0.55	0.44
0.05	9.07	1.49	0.56	0.42
0.06	9.26	1.61	0.56	0.44

TABLE 2

Critical Micelle Concentration and Degree of Micelle Ionization of Aqueous Cetyl Pyridinium Micelles in the Presence of Different Concentrations of PVP K90 and the Standard Gibbs Energy Associated with the Polymer-Surfactant Interaction<sup>a</sup>

% PVP K90	CMC $\times 10^4$ (M)	CMC <sub>p</sub> $\times 10^3$ (M)	$\alpha$	$\alpha_p$	$\Delta G_t^0$ (kJ mol <sup>-1</sup> )
0.001	9.05	1.30	0.54	0.44	-0.35
0.002	9.15	1.30	0.54	0.44	-0.35
0.005	9.16	1.35	0.54	0.43	-0.28
0.01	9.21	1.34	0.53	0.43	-0.25
0.03	9.04	1.28	0.55	0.45	-0.41
0.05	9.20	1.30	0.55	0.45	-0.35
0.07	9.17	1.35	0.53	0.43	-0.34

<sup>a</sup> The standard Gibbs energy is calculated according to Eq. [1].

In the presence of different PVP K90 concentrations, the conductivity curves can be represented by three linear relations, and two breakpoints were also detected. The CMC values deduced from these plots are listed in Table 2. Here, the lower CMC is also ascribed to the pure micelle association and the second cmc, CMC<sub>p</sub>, does not depend on the polymer concentration.

All these facts may indicate that the interaction between cetyl pyridinium chloride and PVP polymers depends on the polymer hydrophobicity; i.e., only high-molecular-weight PVP polymers such as PVP K30 and PVP K90, interact with the surfactant.

In the presence of PEG polymers, the conductivity curves present two CMC values corresponding to different micellar aggregation processes (Fig. 2). Tables 3 and 4 show these data for PEG 20000 and PEG 35000, respectively. The first break corresponds to a CMC close to that of the pure surfactant, so that was associated with the formation of pure micelle. The second CMC was associated with polymer-surfactant aggregates and remains unchanged with increase in PEG concentration.

TABLE 3

Critical Micelle Concentrations and Degree of Micelle Ionization of Aqueous Cetyl Pyridinium Micelles in the Presence of Different PEG 20000 Concentrations and the Standard Gibbs Energy Associated with the Polymer-Surfactant Interaction<sup>a</sup>

% PEG 20000	CMC $\times 10^4$ (M)	CMC <sub>p</sub> $\times 10^3$ (M)	$\alpha$	$\alpha_p$	$\Delta G_t^0$ (kJ mol <sup>-1</sup> )
0.02	9.09	1.32	0.57	0.44	-0.81
0.03	9.09	1.27	0.61	0.46	-1.31
0.045	9.05	1.32	0.57	0.43	-0.98
0.066	9.04	1.31	0.57	0.43	-1.00
0.085	8.99	1.30	0.55	0.43	-0.70
0.10	9.04	1.35	0.55	0.43	-0.83

<sup>a</sup> The standard Gibbs energy is calculated according to Eq. [1].

TABLE 4

Critical Micelle Concentration and Degree of Micelle Ionization of Aqueous Cetyl Pyridinium Micelles in the Presence of Different PEG 35000 Concentrations and the Standard Gibbs Energy Associated with the Polymer-Surfactant Interaction<sup>a</sup>

% PEG 35000	CMC $\times 10^4$ (M)	CMC <sub>p</sub> $\times 10^3$ (M)	$\alpha$	$\alpha_p$	$\Delta G_t^0$ (kJ mol <sup>-1</sup> )
0.01	9.14	1.26	0.58	0.44	-1.16
0.02	8.99	1.26	0.58	0.45	-1.00
0.03	8.93	1.27	0.61	0.48	-1.00
0.04	8.88	1.27	0.59	0.44	-1.24
0.05	8.95	1.26	0.60	0.44	-1.45
0.06	8.94	1.26	0.59	0.44	-1.32
0.07	8.94	1.22	0.62	0.45	-1.48
0.08	9.25	1.24	0.62	0.48	-1.26

All these conclusions are also supported by the fact that slopes before ( $\sim 90$ ), and after ( $\sim 50$ ) the first breakpoint are equal to those in the absence of polymers, indicating that this point is associated with the aggregation of free micelles. The third slope ( $\sim 38$ ) is lower than the other ones and can be associated with the polymer-surfactant aggregates.

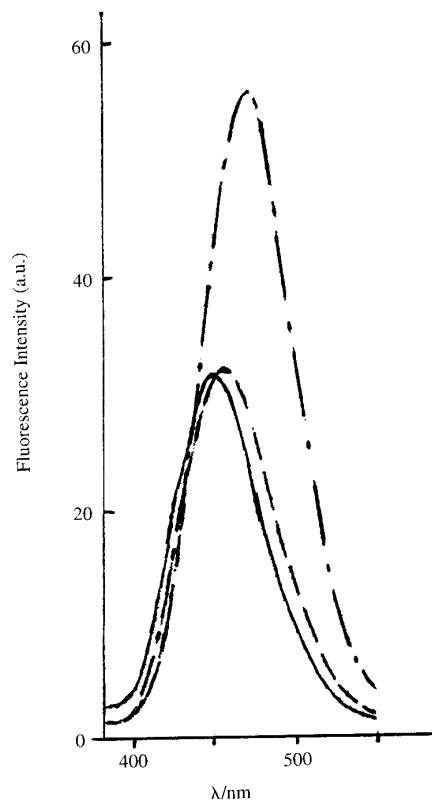


FIG. 3. Fluorescence spectra of pyrene 1-carboxaldehyde solubilized in micelles of cetyl pyridinium chloride and 0.03% PVP K90: —, 2.26 mM Cpy; --, 1.06 mM Cpy; - · -, 0.79 mM Cpy.

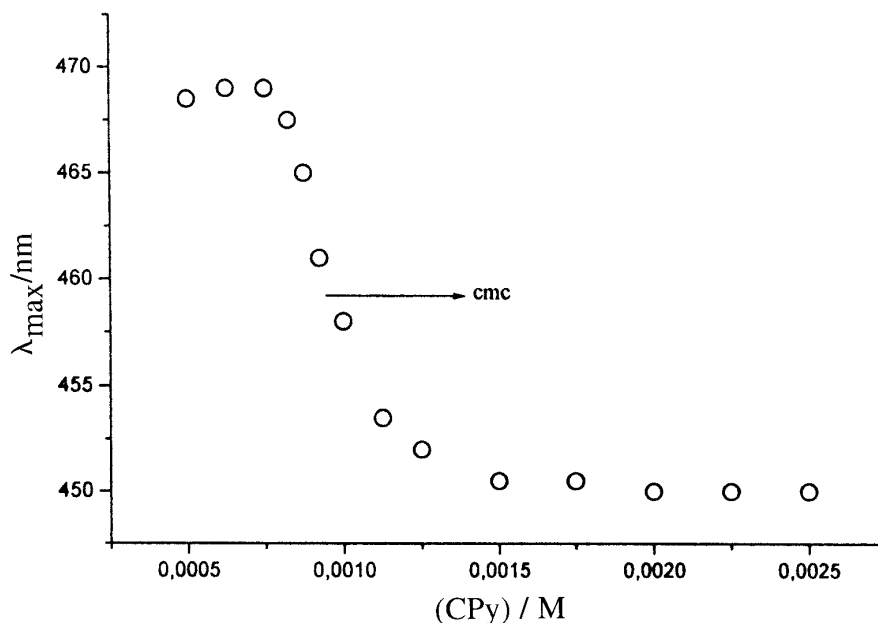


FIG. 4. Variation of  $\lambda_{\max}$  for pyrene 1-carboxaldehyde with cetyl pyridinium chloride concentration.

It is important to consider that all slopes are practically unaffected by both polymer size and polymer concentration.

#### Determination of the Critical Micelle Concentration by Fluorescence Probing

Fluorescence probing has been used to determine the CMC of micelles in the absence and presence of polymers and was also used to estimate the interface polarity of micellar aggregates. The fluorescent probe was pyrene 1-carboxaldehyde, PyCHO.

The fluorescence of this probe strongly depends on solvent polarity; i.e., the fluorescence maximum shows a red shift with increased solvent polarity which is linear with the solvent dielectric constant (16). In addition, NMR studies have shown that this compound is solubilized at the micellar interface (15); as a consequence, the fluorescence of the probe in micelles provides a direct measure of the polarity of the micelle–water interface.

The CMC of micelles can be also determined from emission spectra of PyCHO solubilized in micellar solutions of variable surfactant concentrations with and without polymers. For orientation purposes some of these spectra are represented in Fig. 3.

Figure 4 presents the plot of the position corresponding to the maximum of the PyCHO emission spectrum,  $\lambda_M$ , against surfactant concentration in the absence of polymers. As can be seen in this figure, at surfactant concentrations lower than the CMC, the maximum position is around 469 nm, corresponding to PyCHO aqueous solutions, whereas above the CMC, the fluorescence maximum is blue shifted. This indicates that the fluorescent probe is displaced to a more

hydrophobic environment. When a particular surfactant concentration is reached,  $\lambda_M$  remains constant. The CMC corresponds to the inflection point of this curve and was calculated from the minimum of its first derivative. From this methodology we have obtained for the CMC of pure surfactant the value of  $8.8 \times 10^{-4} M$ , in excellent agreement with that found by conductivity measurements. It is interesting to note that from fluorescence measurements no second breakpoint was detected. This is consistent with conductivity results obtained in this work.

It is also possible to obtain the  $\lambda_M$  of pyrene 1-carboxaldehyde in the micelle and from the linear relation between  $\lambda_M$  and the solvent dielectric constant to estimate the polarity of the micellar interface. In the absence of polymers we found that the dielectric constant of the water–micelle interface was  $35.3 \pm 0.5$ , in agreement with values found by other authors for cationic micelles (20, 21).

To confirm conductivity results the CMCs of micelles with different polymer concentrations were determined by fluorescence probing. The CMC is calculated from the minimum of the first derivative of  $\lambda_M$ -versus-surfactant concentration curves.

All the results are consistent with those from conductivity. In Table 5 are the CMC values determined by fluorescence measurements, and Fig. 5 shows some of these results. Table 5 also presents the interface dielectric constant of aggregates containing polymers, and for comparative purposes the value of the pure micelle is also shown. As can be seen only one discontinuity was detected in curves corresponding to micellar solutions with PVP K15, PVP K25, or low concentrations of PVP K30, whereas two breakpoints were ob-

TABLE 5

**Critical Micelle Concentration and Micelle Interface Dielectric Constant of Aqueous Cetyl Pyridinium Chloride Micelles with and without Polymers Determined by Fluorescence Measurements**

% Polymer	CMC $\times 10^4$ (M)	CMC <sub>p</sub> $\times 10^3$ (M)	$\epsilon$
0	8.8	—	35.3 $\pm$ 0.5
PVP K15			
0.02	9.1	—	35.3 $\pm$ 0.8
0.05	9.1	—	35.4 $\pm$ 0.1
PVP K25			
0.02	9.2	—	35.2 $\pm$ 0.2
0.06	9.4	—	34.8 $\pm$ 0.6
PVP K30			
0.01	9.2	—	35.6 $\pm$ 0.5
0.03	9.3	1.2	32.9 $\pm$ 0.3
0.05	9.8	1.6	32.6 $\pm$ 0.5
0.06	8.8	1.8	33.0 $\pm$ 0.7
PVP K90			
0.03	9.0	1.4	33.6 $\pm$ 0.4
0.05	9.4	1.2	34.5 $\pm$ 1.5
0.07	8.9	1.4	33.6 $\pm$ 0.5
PEG 20000			
0.04	8.5	1.3	31.2 $\pm$ 0.2
0.06	9.4	1.3	32.2 $\pm$ 0.8
0.10	9.1	1.3	32.1 $\pm$ 0.7
PEG 35000			
0.03	9.2	1.6	33.5 $\pm$ 0.3
0.04	9.2	1.2	33.5 $\pm$ 0.5
0.06	9.7	1.5	33.5 $\pm$ 0.2

served in solutions with PVP K90, PEG 20000, PEG 35000, and high concentrations of PVP K30. Examination of the results in Table 5 shows the following: (i) The addition of PVP K15, PVP K25, and low concentrations of PVP K30 does not modify the CMC of aggregates as compared with the pure micelle. The dielectric constant of the micellar interface is practically unaffected by the addition of polymers. These facts show no interactions between these polymers and CPy, in agreement with data from conductivity. (ii) When high PVP K30 concentrations and PVP K90 were added to CPy solutions, two CMC values were determined. On the other hand, the addition of these polymers decreases the interface polarity of polymer-surfactant aggregates with respect to the pure micelle. (iii) In the presence of PEG polymers, plots of  $\lambda_M$  versus surfactant concentration also present two breakpoints corresponding to the aggregation processes of free and polymer-surfactant micelles, respectively. The CMC values agree with those obtained from conductivity curves. The interface polarity, given as the dielectric constant of the micellar interface, weakly decreases with respect to that corresponding to micelles without polymers.

The information obtained from the fluorescence spectra of PyCHO solubilized in micelles with and without polymers revealed that the interaction takes place between PEG poly-

mers or between high-molecular-weight PVP ( $\geq 40,000$  g/mol) polymers and CPy surfactant. The interaction appears at a surfactant concentration higher than the CMC of the micelle without polymers. The polarity of the micelle interface decreases with the addition of polymers. This might indicate that the addition of these polymers increases the size of micelles. This assumption is based on results from other authors who have observed that the increase in micelle size induces a decrease in the area per head group (22) with a simultaneous decrease in the interface polarity (20).

#### *Determination of the Degree of Micelle Ionization and the Standard Gibbs Energy Associated with the Interaction*

To obtain more information about the interaction between these polymers and cetyl pyridinium chloride, the degree of micelle ionization and the standard Gibbs energy associated with the interaction were calculated.

In pure micelles the ionization degree,  $\alpha$ , was determined from the ratio of the slopes of the conductivity-versus-surfactant concentration plots above and below the CMC (7, 23). However, in some polymer-surfactant solutions conductivity curves can be represented by three linear relations, and as a consequence, two ionization degrees were calculated. If  $S_1$ ,  $S_2$ , and  $S_3$  are the conductivity slopes respectively before the CMC, between the CMC and CMC<sub>p</sub>, and above CMC<sub>p</sub>, the first ionization degree,  $\alpha$ , is calculated from the ratio  $S_2/S_1$ , and the second ionization degree,  $\alpha_p$ , from the ratio  $S_3/S_1$ . The calculated  $\alpha$  values are listed in Tables 1-4.

From micelle ionization degrees we conclude the following: (i) The degree of ionization of micelles without polymers,  $\alpha$ , is  $0.53 \pm 0.05$ . This value agrees with values obtained for cationic micelles with the same counterion,  $\text{Cl}^-$ , by other authors (24). (ii) In systems containing PVP K15, PVP K25, or low concentrations of PVP K30, the degree of ionization remains constant around  $0.51 \pm 0.02$ . This value is the same as that of pure micelles. This is an additional argument to confirm no interactions between these polymers and CPy. (iii) When PVP K90, PEG 20000, PEG 35000, or high PVP K30 concentrations were added to surfactant solutions, the first ionization degree was the same as the value for micelles without polymers. The second ionization degree,  $\alpha_p$ , decreased with respect to that corresponding to pure micelles. This value is not affected by either polymer size or polymer concentration. The decrease in  $\alpha_p$  may indicate an increase in the micelle size induced by polymers. This is consistent with the decrease in interface polarity detected by fluorescence probing.

We have also calculated the standard free energy associated with the interaction between surfactant and polymers,  $\Delta G_i^0$ , given by the difference in the Gibbs free energy of transfer of the surfactant monomer from aqueous solution to the micelle in the presence and in the absence of polymers; that for monovalent counterions is (25, 26)

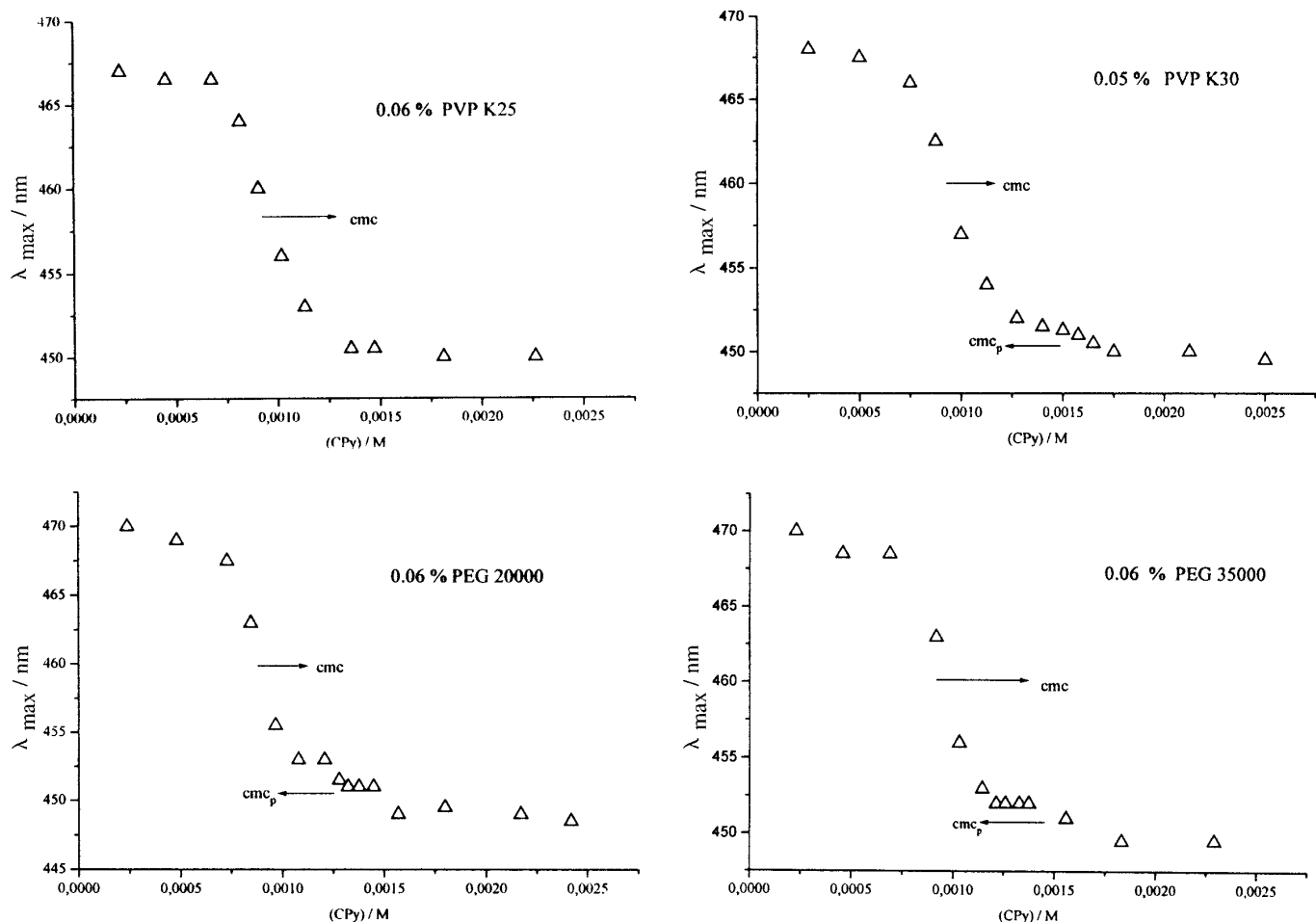


FIG. 5. Variation of  $\lambda_{\max}$  for pyrene 1-carboxaldehyde with cetyl pyridinium chloride concentration for micellar solutions with polymers.

$$\Delta G_t^0 = RT[(2 - \alpha_p) \ln CMC_p - (2 - \alpha) \ln CMC], \quad [1]$$

where the subscript p refers to polymer-surfactant aggregates. The standard Gibbs energy calculated by Eq. [1] and the CMCs and ionization degrees obtained in this work are summarized in Tables 2-4.

The results show that  $\Delta G_t^0$  remains constant with polymer concentration. The average values were  $-0.33 \pm 0.05$ ,  $-0.90 \pm 0.19$ , and  $-1.24 \pm 0.16$  kJ/mol, for micellar solutions containing PVP K90, PEG 20000, and PEG 35000, respectively. The standard Gibbs energy of micelles containing PVP K30 was not calculated because there is evidence of several processes besides micellar aggregation, as can be deduced from the linear dependence between  $CMC_p$  and polymer concentration. Thus,  $CMC_p$  values do not correspond to a true critical micelle aggregation and, as a consequence, cannot be used in Eq. [1].

$\Delta G_t^0$  values for the interaction of PVP K90 with SDS and  $\text{Cu}(\text{SD})_2$  are  $-4.6$  and  $-2.7$  kJ/mol (26), respectively. On the other hand, values corresponding to the interaction be-

tween these surfactants and PEO (26) are  $-2.7$  and  $-1.2$  kJ/mol for SDS and  $\text{Cu}(\text{SD})_2$ , respectively. These values are smaller than those corresponding to the interaction with CPy, except in the case of PEG 35000. This indicates that these anionic surfactants generally interact more strongly with polymers than CPy.

In all cases the free energy for transfer of the surfactant monomer toward the polymer-surfactant micelle is smaller than the value corresponding to pure micelles, indicating that the addition of these polymers stabilizes the micelle. The stabilization can be due to the decrease in the degree of ionization induced by polymer addition. The micelle stabilization is more pronounced in PEG solutions. This can be explained if it is considered that PEG polymers are more hydrophilic than PVP polymers. Thus, the attraction between the surfactant head group and polymer segments becomes important, giving a favorable contribution to the free energy of polymer-surfactant micelles formation (27). In contrast, a weak interaction between hydrophobic PVP polymers, PVP K30 and PVP K90, and CPy was observed. In these

cases the attraction between the hydrophobic surfactant region and the polymer molecule seems to be responsible for the interaction. From these results it can be concluded that the polymer's hydrophilic-lipophilic balance is responsible for its interaction with a given surfactant.

### SUMMARY

The above results show that high-molecular-weight PVP polymers and PEG polymers can interact with cetyl pyridinium chloride cationic surfactant. However, low-molecular-weight PVP polymers do not interact with this surfactant. These facts agree with the conclusions of other authors who found that the polymer's hydrophilic-lipophilic balance determines its interaction with a given surfactant.

Results obtained in this work show that the interaction results in the formation of polymer-surfactant micelles with a degree of ionization smaller than that of free micelles. The aggregation of polymer-surfactant micelles takes place at a surfactant concentration,  $CMC_p$ , higher than the critical micelle concentration of micelles without polymer, and the addition of these polymers decreases the polarity of the micelle interface.

### ACKNOWLEDGMENT

The authors acknowledge the Junta de Castilla y León for financial support of this project (Project SA 05-95).

### REFERENCES

- Breuer, M. M., and Robb, I. D., *Chem. Ind.*, 530 (1972).
- Goddard, E. D., *Colloids Surf.* **19**, 255 (1986).
- Thalberg, K., and Lindman, B., in "Interactions of Surfactants with Polymers and Proteins"; (E. D. Goddard and K. P. Ananthapadmanabhan, Eds.), p. 203. CRC Press, Boca Raton, FL, 1993.
- Brackman, J. C., and Engberts, J. B. F. N., *Chem. Soc. Rev.* **22**, 85 (1993).
- Witte, F. M., Buwalda, P. L., and Engberts, J. B. F. N., *Colloid Polym. Sci.* **265**, 42 (1987).
- Horin, S., and Arai, H., *J. Colloid Interface Sci.* **32**, 547 (1970).
- Zana, R., Lianos, P., and Lang, J., *J. Phys. Chem.* **89**, 41 (1985).
- Brackman, J. C., and Engberts, J. B. F. N., *Langmuir* **7**, 2097 (1991).
- Winnik, F. M., Winnik, M. A., and Tazuke, S., *J. Phys. Chem.* **91**, 594 (1987).
- (a) Thalberg, K., Lindman, B., and Karlström, G., *J. Phys. Chem.* **94**, 4289 (1990); (b) **95**, 6004 (1991); (c) Thalberg, K., and Lindman, B., *Langmuir* **7**, 277 (1991).
- (a) Chu, D., and Thomas, J. K., *J. Am. Chem. Soc.* **108**, 6270 (1986); (b) Almgren, M., Hansson, P., Mukhtar, E., and van Stam, J., *Langmuir* **8**, 2405 (1992); (c) Hansson, P., and Almgren, M., *Langmuir* **10**, 2115 (1994).
- Ruckenstein, E., Huber, G., and Hoffmann, H., *Langmuir* **3**, 382 (1987).
- White, F. R., and Engberts, J. B. F. N., *Colloids Surf.* **36**, 417 (1989).
- Maltesh, C., and Somasundaran, P., *J. Colloid Interface Sci.* **157**, 14 (1993).
- Eriksson, J. C., and Gillbert, G., *Acta Chem. Scand.* **20**, 2019 (1966).
- Kalyanasundaram, K., and Thomas, K. L., *J. Phys. Chem.* **81**, 2176 (1977).
- Lind, J. E., Zwoleni, K. J. J., and Fuoss, R. M., *J. Am. Chem. Soc.* **81**, 1557 (1959).
- Treiner, C., and Makayssi, A., *Langmuir* **8**, 794 (1992).
- Rosen, M. J., in "Surfactant and Interfacial Phenomena," p. 96. Wiley, New York, 1978.
- Zachariasse, K. A., Phuc, N. N., and Kozankiewick, K., *J. Phys. Chem.* **85**, 2676 (1981).
- Fernandez, M. S., and Fromherz, J., *J. Phys. Chem.* **81**, 1755 (1981).
- Tanford, C., in "The Hydrophobic Effect," 2nd ed., p. 53. Wiley, New York, 1980.
- Zana, R., Binana-Limbelé, W., Kamenka, N., and Lindman, B., *J. Phys. Chem.* **96**, 5461 (1992).
- Sepulveda, L., and Cortés, J., *J. Phys. Chem.* **89**, 5322 (1985).
- Hunter, R. J., in "Foundation of Colloid Science," Vol. 1, p. 596. Oxford, Oxford, 1987.
- Kamenka, N., Burgaud, I., Treiner, C., and Zana, R., *Langmuir* **10**, 3455 (1994).
- Nagarajan, R., *J. Chem. Phys.* **90**, 1980 (1989).