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Tensiometric behavior of [P4VPC8-20-SDS] poly(N-octyl-4-vinylpyridinium bromide)(20%)/sodium dodecylsulfate system in aqueous solution - Influence of NaCl salt

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ABSTRACT

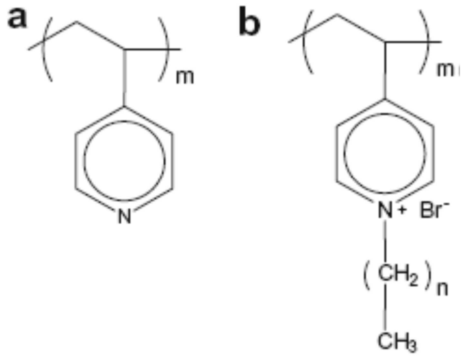
*In this work, we consider the tensiometric behavior of the system poly(N-octyl-4-vinylpyridinium bromide)(20%)/sodium dodecylsulfate [**P4VPC8-20-SDS**] in absence and the presence of NaCl salt. Thus, the copolymer poly(N-octyl-4-vinylpyridinium bromide)(20%) [**P4VPC8-20**] is used under quaternization rate of 20%. The results show that the copolymer concentration plays a main role in the tensiometric behavior of this system. Also, the salt addition decreases the surface tension of the solution. Finally, the surface tension of the solution decreases as a function of the SDS concentrations for all the copolymer concentrations. All the results confirm the main role of the electrostatic interactions and the importance of the copolymer character in term of the hydrophobic/hydrophylic balance.*

Key words: Tensiometry, Poly(N-octyl-4-vinylpyridinium bromide)(20%) **P4VPC8-20**, Sodium dodecylsulfate, NaCl salt, Interactions.

INTRODUCTION

The polymer/surfactant mixtures are used in a wide range of commercial applications, and the study of their behavior in the bulk and at the interface is of great interest [1-3]. The main types interactions of polymers/surfactant can be gathered in a relatively weak interactions between the polymer chains and the surfactant, or the strong electrostatic interactions between the opposit charge polyelectrolytes and the charged groups of the surfactant [4].

Experiences on the polymer/surfactant mixture are simply concentred on their properties in solution. But until now, interfacial properties of these systems are considerably less accessible. The present paper describes the amphiphile structure of the copolymer based on poly(N-octyl-4-vinylpyridinium bromide)(20%) **P4VPC8-20** under quaternization rate of 20%, mixed with the anionic surfactant **SDS.** The tensiometric experimental mesurements show that the physicochemical properties in aqueous solution and in absence and in the presence of NaCl salt, are related with the copolymer behavior.



Scheme 1. Structural unit of P4VP and P4VP-C_8Br (a) P4VP, (b) P4VPC8-20, with n = 8

MATERIALS AND METHODS

2.1. Preparation of the mother solution of P4VPC8-20:

To obtain a mother solution of the copolymer **P4VPC8-20** with a concentration of 10^3 mg/lit.. an amount of 0.05 g of this copolymer is introduced into a 50ml volumetric flask and completed by 50ml of a double distilled water. The solution is stirred for 24 hours at room temperature and then filtered using ordinary filter paper. Various concentrations of the copolymer (10, 20, 50 et 80 mg/lit.) have been prepared by dilution from the mother solution.

2.2. Preparation of the mother solution of Sodium dodecylSulphate (SDS):

In a 50 ml volumetric flask, we dissolve 2.88 g of the SDS in double distilled water under agitation to obtain an aqueous solution with the concentration of 2.10^{-1} M. A very homogeneous solution is obtained.

2.3- Preparation of the salt solution:

A solution of sodium chlorid NaCl with a concentration of 0.1 M is prepared. For this effect, we dissolve 5.85g of the salt in a 100ml of double distilled water in a volumetric flask.

RESULTS AND DISCUSSION

2.1 Tensiometric study of the SDS in absence and in the presence of NaCl

In this part of work, we are interested to study the variation of the surface tension of sodium dodecylsulfate (SDS) aqueous solution as a function of its concentration with and without added salt NaCl at T=25 °C.

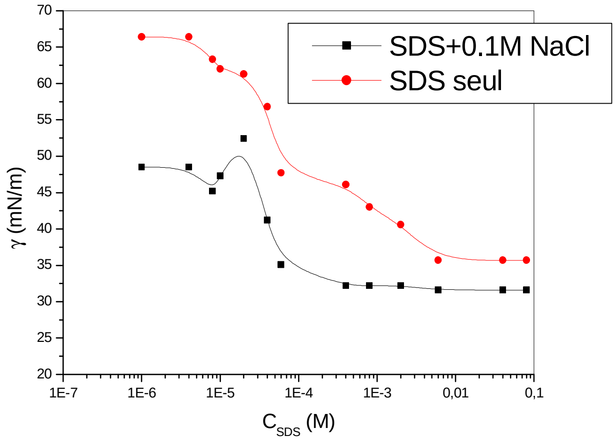


Figure 1: Surface tension variation of sodium dodecylsulfate(SDS) aqueous solutions as a function of its concentration with and without added NaCl at T=25 °C

The previous figure shows the variation of the surface tension of sodium dodecylsulfate (SDS) as a function of its concentration with and without NaCl. On the figure 1, the variation of the tension surface decreases in the interval SDS concentration [10^{-6} M -6×10^{-3} M], then stabilizes beyond of this concentration. The concentration 6×10^{-3} M is called critical micelle concentration (CMC). Indeed, the curve slope of the tension surface variation with the SDS concentration, in the presence of the NaCl salt is different to that of SDS alone. We observe also a pic in the range concentration of SDS [7×10^{-6} M - 4×10^{-5} M]. This is explained by the presence of NaCl which predominates the electrostatic repulsions compared to the hydrophobe-hydrophobe interactions. We can say that the adsorption of the hydrophobe part at the water-air interface will be difficult. In the SDS concentration domain [4×10^{-5} M -$3,8\times10^{-4}$ M], the surface tension variation decreases rapidly then it stabilizes beyond this domain.

The addition of the salt reduces the superficial tension of the solution, such as $\gamma = 65$ mN/m (for the SDS alone) and $\gamma = 48.46$ mN/m (for the (SDS + NaCl)). From this first study, we can conclude that the salt addition promotes the surfactant micellization. **CMC_{SDS}** $= 6\times10^{-3}$ M is comparable with the litterature results [5-7] .

2.2 Tensiometric study of P4VPC8-20-SDS mixture in absence of NaCl

The Figure 2 shows the surface tension variation of aqueous solutions of the copolymer poly(N-octyl-4-vinylpyridinium bromide)(20%) **P4VPC8-20**, as a function of the added SDS at copolymer concentrations respectively equal to 0 ppm, 10 ppm, 20 ppm, 50 ppm et 80 ppm.

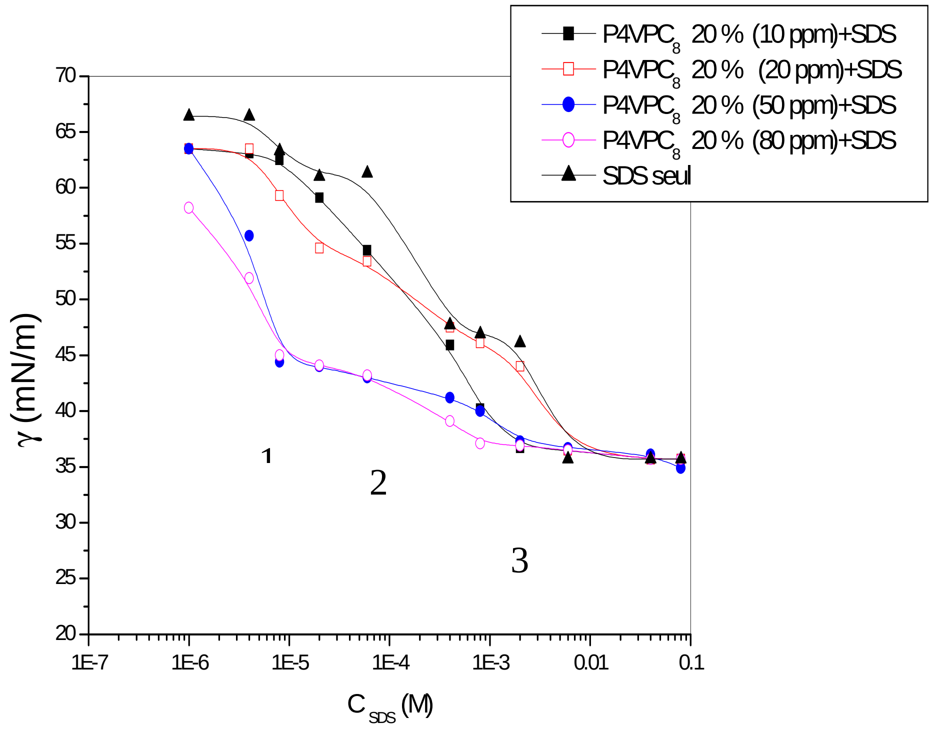


Figure 2: Surface tension variation of aqueous solutions with the copolymer poly(N-octyl-4-vinylpyridinium bromide)(20%) P4VPC8-20, as function of the added SDS, for copolymer concentrations 0ppm, 10ppm, 20ppm, 50ppm et 80 ppm, at T=25 °C

We remark that the surface tension of the solution decreases as a function of the SDS concentration, for all the copolymer concentrations. The copolymer addition to the solution decreases the surface tension. This is explained by the less adsorption of the copolymer hydrophobe part at the water-air interface. At a constant SDS concentration, the surface tension decreases according to the copolymer concentration. This means that when the copolymer concentration increases, the surface tension of the solution decreases.

For the copolymer concentration value 10 ppm, the curve slope of the surface tension variation of the solution is comparable to that of the SDS alone. In the domain [10^{-6} M - 7.98×10^{-6} M] of SDS concentration, we remark a platform, then a sharp decrease in the interval of SDS concentration [7.98×10^{-6} M - 0.0019 M]. The point which corresponds to the slope change is called “Critical Aggregation Concentration” **(CAC)** (beginning of the micelles formation on the polymer) [8]. In the domain [0.0019 M - 10^{-1} M], the surface tension diminution is more or less constant. The polymer is saturated with the micelles, and consequently the free micelles formation appears in the solution [8].

Concerning the copolymer concentration 20ppm, we observe a platform in the concentration domain [10^{-6} M - 3.95×10^{-6} M] (formation of free micelles in the solution). Then, a fall of the surface tension in the concentration domain [3.95×10^{-6} M - 2×10^{-5} M], where the beginning of the micelles formation on the polymer **(CAC).** In the SDS domain concentration [2×10^{-5} M - 0.01 M], the surface tension weakly decreases, because the copolymer is saturated with the micelles.

For the concentration 50ppm, the copolymer present a good surfactant behavior basing on the littérature result [8]. In the concentration domain [10^{-6} M - 8.89×10^{-6} M], we observe a sharp decrease of the surface tension. Indeed, this fall gets back at the adsorption of the hydrophobic segments at the water-air interface. In the domain [8.89×10^{-6} M - 8.45×10^{-4} M], the variation of the surface tension as a function of the SDS concentration decreases slightly. This is explained by the beginning of the micelles formation on the copolymer. In the concentrations domain of SDS [8.45×10^{-4} M - 0.0019 M], the variation of the surface tension in the solution decreases slightly, and it stabilizes beyond this field. The polymer is saturated with the SDS molecules, and the formation of free micelles in solution begans.

In the case where the copolymer concentration equal to 80 ppm, we observe a surface tension fall, in the concentration domain of SDS [10^{-6} M - 7.89×10^{-6} M]. Then the surface tension diminution becomes weak in the concentration interval [7.89×10^{-6} M - 5.87×10^{-5} M]. Indeed, the micelles start surrounding polymeric chains at the concentration 7.89×10^{-6} M which is called “critical agregation concentration” **(CAC).**

The surface tension diminution of the solution becomes remarkable in the domain [5.87×10^{-5} M - 8×10^{-4} M], and beyond of this concentration, the variation stabilizes. The concentration 8×10^{-4} M is called “critical micellar concentration” **(CMC)**, where the formation of free micelles in solution begans.

At weak copolymer concentrations and at constant SDS concentration, the surface tension of the solution decreases as a function of the copolymer concentration. This is represented by the following equation:

$$\gamma_{SDS} > \gamma_{10ppm} > \gamma_{20ppm} > \gamma_{50ppm} > \gamma_{80ppm}$$

3.3.1. Tensiometric study of P4VPC8-20-SDS mixture in presence of NaCl

The figure 3 shows the tension surface variation of 0.1 M NaCl aqueous solutions of the copolymer poly(N-octyl-4-vinylpyridinium bromide) (20%) **P4VPC8-20**, as a function of the added SDS at the copolymer concentrations, respectively 0 ppm, 10 ppm, 20 ppm, 50 ppm and 80 ppm. The representative curves have different shapes compared to that represented in the previous figure 2.

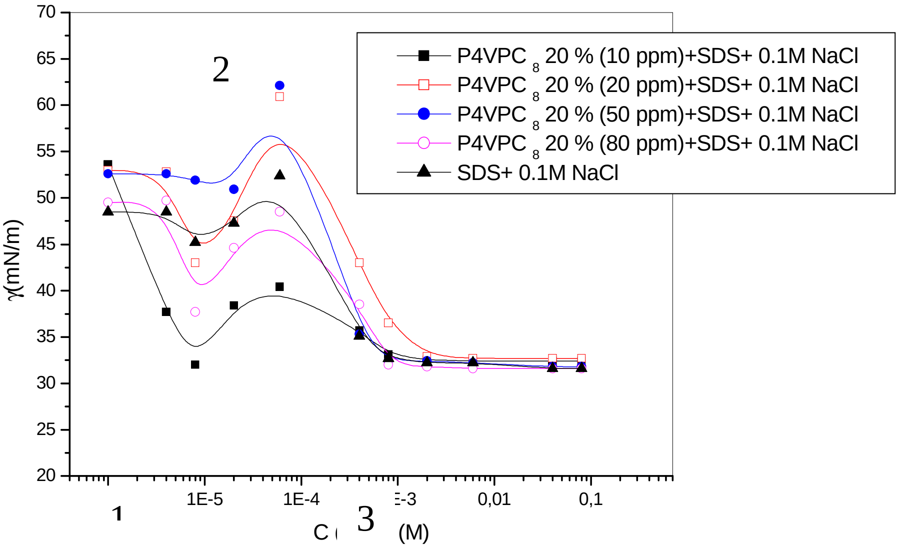


Figure 3: Surface tension variation of 0.1 M NaCl aqueous solutions with the copolymer poly(N-octyl-4-vinylpyridinium bromide)(20%) P4VPC8-20, as a function of the added SDS, for copolymer concentrations 0 ppm, 10 ppm, 20 ppm, 50 ppm et 80 ppm

In the SDS concentration interval [10^{-6} M - 8.13×10^{-6} M], the surface tension of the solution decreases as a function of SDS concentration. This is due to the adsorption of the surfactant molecules on the copolymer chains. This adsorption can be produced at very weak concentrations of the surfactant.

Over the first zone **(1)**, the surfactant and the copolymer are adsorbed togather at the surface producing weak interactions between them [9]. Beyond the first zone **(1)**, we observe an increasing in the surface tension until the SDS concentration equal to 6.28×10^{-5} M (**CAC**) where the second zone **(2)** begans. Indeed, the copolymer starts to desorb from the interface water-air of the solution.

In the domain of SDS concentration [6.28×10^{-5} M - 9.17×10^{-4} M], the surface tension decreases, then it stabilizes beyond this interval. At this second zone, the formation of agregats takes place and the surfactant micelles are attached to the copolymer chains. The stabilization of the surface tension during the third zone is due to the polymer saturation by the micelles and to the formation of free micelles in solution [8]. Our results are comparable to the literature data [8-10]. The **CMC** does't depend on the copolymer concentration, but it slightly increases.

The variation of the surface tension of 0.1 M NaCl aqueous solutions with the **SDS** concentration, is different from that of the **SDS** alone. In fact, the NaCl salt leads to a general fall in the surface tension of the system at all concentrations of the surfactant. NaCl has a strong effect on the copolymer conformation. In the other hand, the surface tension curves show a maximum and minimum showing that the solution self-re-organizes as a function of the **SDS** concentration. This behaviour is due to the presence of salt that predominates the repulsives electrostatiques interactions and precisely into the copolymer.

The analysis of these results shows that the surface tension of 0.1 M NaCl aqueous solutions, doesn't vary regularly as a function of the copolymer concentration.

In the domain of SDS concentration [10^{-6} M - 1.42×10^{-5} M], the surface tension of the solution decreases as a function of the SDS concentration. This is due to the organization of the surfactant and the copolymer at the water-air interface, producing a weak interactions between them. In the domain of SDS concentration [1.42×10^{-5} M - 6×10^{-5} M], the surface tension of the solution increases as a function of the SDS concentration. This is explained by the desorption of the copolymer from the water-air interface. We also observe a decreasing of the surface tension of the solution in the domain [6×10^{-5} M - 8×10^{-4} M], and beyond of this interval the surface tension of the solution stabilizes. This decreasing in the surface tension is due to the formation of agregates micelles/copolymer, and the stabilization is explained by the formation of free micelles in the solution after the saturation of the copolymer by the micelles.

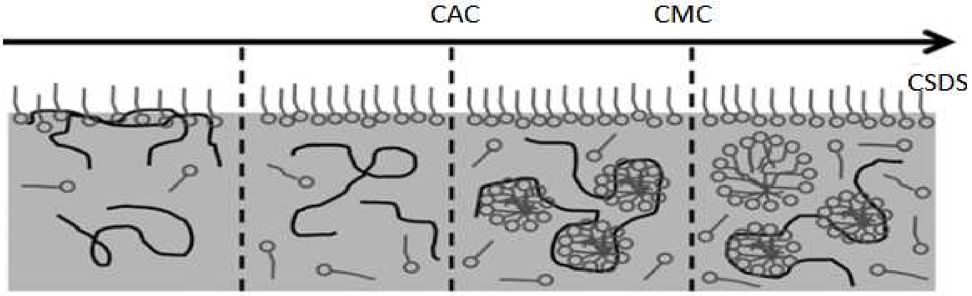


Figure 4: interactions steps between the polymeric chains and the surfactant molecules [11]

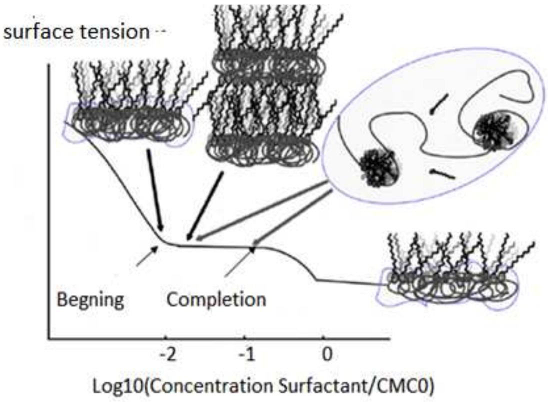


Figure 5: scheme of the evolution of the polymer-surfactant interactions and the surface tension variation for the system of this type [12-14]

The studied system follows the behavior showed in the figure 5 and it was described by Penfold. J. and al. [12-14]. The surface tension variation of this system is characterized by a continued decreasing in the surface tension which is due to the formation of agregates micelles/copolymer. The stabilization intervals are explained by the formation of free micelles in the solution and by the saturation of the copolymer by the micelles.

CONCLUSION

The tensiometry results show that the copolymer **P4VPC8-20** mixed with the SDS in aqueous solution, is a good surfactant system. The copolymer sample **P4VPC8-20** (20%) shows a middle character surfactant following probably to its ratio hydrophobe/hydrophile. The addition of the salt NaCl causes a rapid fall of the tensiometric effect of this system in aqueous solution. In fact, this inorganic salt favorises the micellisation of the SDS. We can also note that the copolymer doesn't reduce enough the surface tension of the solution, in the presence of the salt. These results are explained by the electrostatic interactions and by the hydrophobic /hydrophilic balance.

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