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Research Article

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Ternary system (surfactant-polyelectrolyte-polyelectrolyte) complexes: Determination of the characteristic concentrations

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ABSTRACT

The system (sodium dodecyl sulfate (SDS)-hydrolyzed polyacrylamide AD37-poly(4-vinylpyridine (P4VP)) in aqueous media for the fixed AD37 concentration at T=25°C, was investigated using conductivity measurements. The characteristic concentrations of the surfactant-polyelectrolyte-polyelectrolyte complexation: the critical aggregation concentration (CAC) and saturation of the polyelectrolyte complex (AD37/P4VP) by SDS (X2) were determined from the curve of conductivity according the concentration of surfactant. In the presence of the complex (AD37/P4VP), the relationship between conductivity and SDS concentrations shows two breaks of slope.

Keywords: Complex, conductivity, polyelectrolyte, SDS, CAC, X2

INTRODUCTION

Polymer–surfactant interactions have attracted a great deal of attention for the benefit that the combination of these molecules can provide in several industrial applications [1–3]. Ionic surfactants can strongly interact with oppositely charged polyelectrolytes to form micelle-like structures at a very low critical aggregation concentration (CAC), which is usually a few orders of magnitude lower than the critical micellization concentration (CMC) of the free surfactant [4–7]. This is attributed to the electrostatic attraction between the surfactant and the polyelectrolyte, as well as to the hydrophobic interaction between the surfactant tails. In a surfactant/polyelectrolyte solution, the addition of salt is expected to have a significant effect on their interactions. It has been shown that the addition of salt reduces the strength of electrostatic interaction between surfactants and polyelectrolytes, which results in a larger CAC [8–13].

Hydrolyzed polyacrylamide is a very important water-soluble polymer, which is used as a thickener or modifier for use in the formulations of tertiary oil recovery [14]. Polyvinylpyridines have interesting chemical properties thanks to the nitrogen atom of the aromatic nucleus [15]. Sodium dodecyl sulfate (SDS) is an anionic surfactant generally used to increase lifespan of foams or as detergent, which explains its presence in many cosmetic products such as the shampoos and the toothpastes like in the majority of the detergents with crockery and detergent [16]. In a previous paper [17] the effect of the neutralization degree (α) on the viscosimetric behaviour of (hydrolyzed polyacrylamide, AD37–poly(4-vinylpyridine), P4VP) complex in aqueous solution and in the presence of sodium dodecyl sulphate (SDS) (CMC=0.249 % of SDS [17]) was studied. Physicochemical results show that neutralization degree has an important effect on reduced viscosities values of (AD37–P4VP–SDS) system that reveals the electrostatic and hydrophobic interactions.

The aim of the present work is to study the interactions in aqueous media between the anionic surfactant sodium dodecyl sulfate (SDS) and the polyelectrolyte complex (AD37/P4VP) [18] as a function of neutralization degree (α), using conductivity methods.

EXPERIMENTAL SECTION

Products

Copolymer AD37 based on hydrolyzed acrylamide was provided from Rhône-Poulenc Company (France). Its content in carboxylate function is 27 % and is determined by ^{13}C NMR and potentiometry. Its molar mass is estimated to 5x10^{6} g mol^{-1} by light scattering technique [18, 19]. P4VP polymer was synthesized by radical polymerization. In its neutral form, it is not soluble in water at neutral pH. Nevertheless, its highly polar character induces good solubility in polar organic solvents like DMSO, DMF, methanol or ethanol. Its molar mass is estimated at 4x10^{4} g mol^{-1}, by viscosimetry.

Apparatus

Our conductimetric measurements were made using a conductivity meter CDM 210 (Radiometer, Meter Lab). The solutions studied are contained in a glass cell thermostated double-walled (25□± 0.1) ° C using a heating circulator.

RESULTS AND DISCUSSION

Influence of the (AD37-P4VP) complex on the micellization of SDS surfactant

The ternary system (SDS-P4VP-AD37) was characterized by conductometric measurements. We performed our measures in the continuous phase in SDS concentrations not exceeding 1%, measured pH was around 7.

The same approach was followed by varying the P4VP concentrations for the neutralization degrees $\alpha = 0.1$, 0.2, and 1, respectively. The concentration of the AD37 was held fixed and estimated at 10^{-4} g/ml (Fig. 1, 2 and 3).

For a given degree of neutralization, the critical aggregation concentration increases with increase in the concentration of the P4VP, that is to say, the beginning of the interaction of SDS with P4VP is disadvantaged at high concentrations in P4VP because in the latter case the complexation of P4VP chains with those of the AD37 is favored. When the neutralization degree increases (Fig. 2 and 3), the gap between the curve is more pronounced, higher conductivity values are recorded, since the loading rate (pyridinium ion) increases.

In the presence of the complex (AD37-P4VP) (Fig. 1, 2, and 3), the relationship between conductivity and SDS concentrations shows two breaks of slope. In the classical profiles of the conductivities investigations of polymer-surfactant mixtures, these breaks are related in the interaction between surfactant and polymer nicknamed often the critical aggregation concentration, symbolized by CAC and the concentration of saturation of polymer noted X2. The CAC is always lower than the CMC [20], implying that the formation of polymer-surfactant complex is energetically more favorable than the formation of micelles [21].We note that the complex (AD37-P4VP) causes a linear increase of the conductivity of the system, (Fig. 1, 2 and 3), this increase is even more important when the concentration of both polymers increases. It has been suggested Winnik and al. [22] that for the system (SDS-poly(ethylene imine)), the increase in conductivity of the polymer-surfactant system can be explained in terms of the higher mobility of the sodium ion of SDS bound to the polymer compared with its allocation to SDS micelles in the absence of the polymer. In addition, the polymer-surfactant may be composed of the surfactant micelles bound to the polymer, allowing a higher mobility of the sodium ions of a micelle to another. After reaching the CAC, there is an obvious decrease in the slope caused by the reduction of the mobility of the free ions of surfactant in solution which are hampered before the formation of aggregates bound to the polymer. Free ions SDS more contribute to the conductivity of the solution, compared to the same ions in the micelles [23].

This interaction continues until the saturation of the complex (AD37-P4VP) with SDS, which can be determined by a second break that is the concentration of saturation of polymer. With increasing the SDS concentration, the conductivity dependence is again linear. Between the CAC and X2, there is the area of interaction, i.e. the binding of the SDS molecules to the complex, we observe a non-linear dependence. It has been suggested [23] that the non-linearity could be related to a step in the process of interaction that corresponds to the saturation of the available sites in the complex with the monomers surfactant or micelles of low aggregation number, after this, micelles with larger aggregation number can be formed.

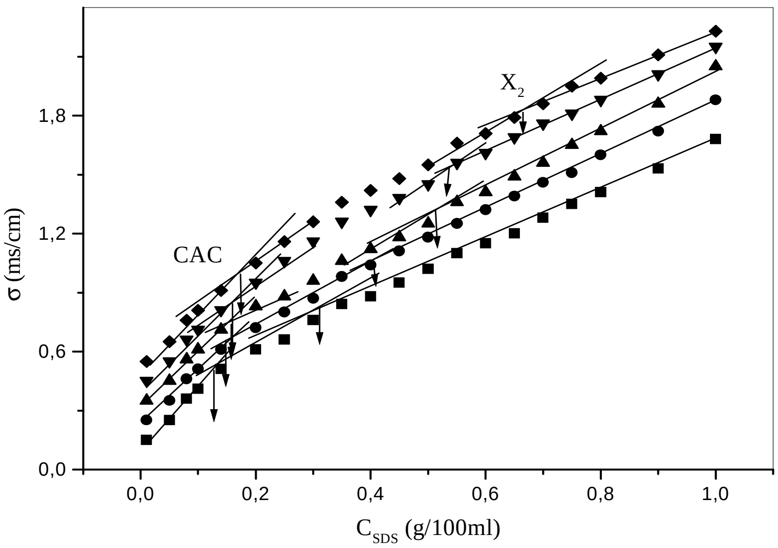

Fig. 1 Change in conductivity of SDS on its concentration at T = 25 ° C, in the presence of the various concentrations in P4VP (g/ml): (■) 0.1x10^{-4}; (●) 0.5x10^{-4}; (▲) 1x10^{-4}; (▼) 2x10^{-4}; (♦) 4x10^{-4}, for α=0.1 and at C_{AD37} =1x10^{-4}g/ml

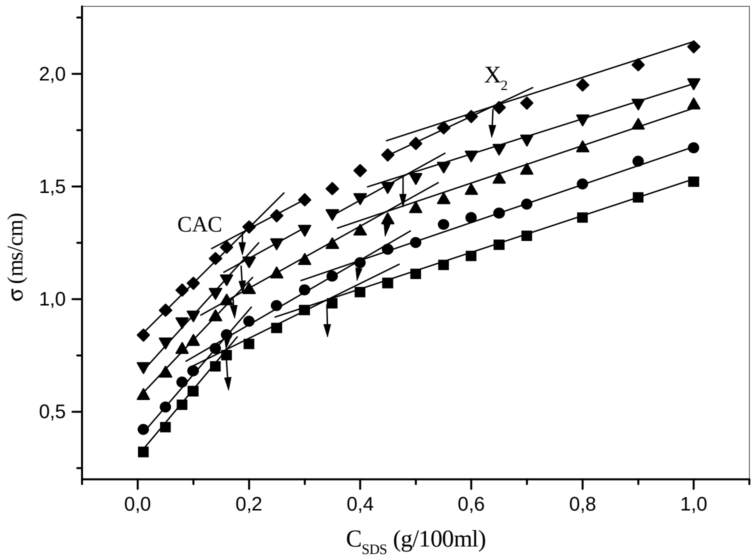

Fig.2 Change in conductivity of SDS on its concentration at T = 25 ° C, in the presence of the various concentrations in P4VP (g/ml): (■) 0.1x10^{-4}; (●) 0.5x10^{-4}; (▲) 1x10^{-4}; (▼) 2x10^{-4}; (♦) 4x10^{-4}, for α=0.5 and at C_{AD37} =1x10^{-4}g/ml

Table 1. give the values of the characteristic concentrations (CAC and X2) as a function of P4VP concentrations for the three neutralization degrees, the concentrations are represented in g / 100 ml.

C_{P4VP}	α = 0.1		α = 0.5		α = 1	
	CAC	X_2	CAC	X_2	CAC	X_2
0.001	0.127	0.31	0.153	0.32	0.161	0.33
0.005	0.13	0.42	0.164	0.35	0.173	0.35
0.01	0.138	0.5	0.172	0.43	0.18	0.4
0.02	0.16	0.55	0.18	0.51	0.195	0.46
0.04	0.17	0.77	0.183	0.72	0.21	0.67

Table 1. Characteristic concentrations (CAC and X2) as a function of P4VP concentrations for the three neutralization degrees

By analyzing the data listed in Table 1, we observe that for a given concentration of P4VP the CAC values increase with the neutralization degree, this is explained by the increasing of the hydrophobicity of P4VP chains when the neutralization degree decrease, in this case the surfactant aggregates can be binding to hydrophobic segments of P4VP. The interaction is therefore favored for low P4VP concentrations with a high hydrophobicity.

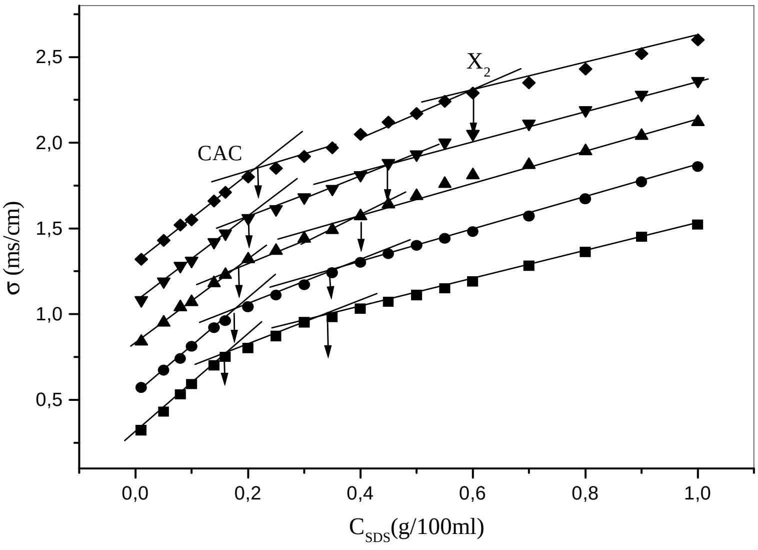

Fig.3 Change in conductivity of SDS on its concentration at T = 25 ° C, in the presence of the various concentrations in P4VP (g/ml): (■) $0.1x10^{-4}$; (●) $0.5x10^{-4}$; (▲) $1x10^{-4}$; (▼) $2x10^{-4}$; (♦) $4x10^{-4}$, for α=1 and at $C_{AD37} = 1x10^{-4}$g/ml

CONCLUSION

This study showed that this system forms a complex in aqueous media. The measurements allowed the determination of the SDS concentration at which the polyelectrolyte complex –SDS interaction begins (CAC) and ends (X2). Between the CAC and X2, there is the area of interaction, i.e. the binding of the SDS molecules to the complex, we observe a non-linear dependence. Thus, the interaction is therefore favored for low P4VP concentrations with a high hydrophobicity.

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REFERENCES

[1] ED Goddard, KP Ananthapadmanabhan. Interactions of Surfactants with Polymers and Proteins, 1st Edition, CRC Press, Boca Raton, FL, **1993**, 172.
[2] S Guillot; D McLoughlin; N Jain; M Delsanti; D Langevin, *Physic J. Condens. Matter.*, **2003**, 15, 230.
[3] B Jönsson, B Lindman, K Holmberg, B Kronberg. Surfactants and Polymers in Aqueous Solution, Wiley, West Sussex, **1998**.
[4] M Almgren; P Hansson; E Mukhtar, *Van Stam J. Langmuir.*, **1992**, 8, 2405.
[5] H Arai; M Murata; K Shinoda, *Colloid Interface Sci. J.*, **1971,** 37, 223.
[6] ED Goddard; RB Hannan, *Colloid Interface Sci. J.*, **1976**, 55 ,73.
[7] M Murata; H Arai, *Colloid Interface Sci. J.*, **1973,** 44, 475.
[8] K Hayakawa; JCT Kwak, *Phys. Chem. J.*, **1982**, 86, 3866.
[9] K Hayakawa; JCT Kwak, *Phys. Chem. J.*, **1983**, 87, 506.
[10] A Malovikova; K Hayakawa; JCT Kwak, *Phys. Chem. J.*, **1984**, 88, 1930.
[11] P Hansson; M Almgren, *Phys. Chem. J.*, **1995,** 16, 684.
[12] C Wang; KC Tam, *Langmuir*, **2002**, 18, 6484.
[13] C Wang; KC Tam; RD Jenkins; CB Tan, *Phys. Chem. B, J.*, **2003**, 107, 4667.
[14] ND Truong, PhD thesis, Strasbourg, France, **1984**.
[15] M Yoshida; N Sakamoto; K Ikemi; S Arichi, *Bull Chem. Sot. Japan*, **1992**, 65, 3108.
[16] JL Salager. Surfactifs types & usages, Universidad of Los Andes, Mérida, **2002**.
[17] L Tennouga; K Medjahed; A Mansri; J Desbrières, *Polym. Bull.*, **2012**, 1, 0783.
[18] A Mansri; L Tennouga; J Desbrières, *Eur. Polym J.*, **2007**, 43, 540–549.
[19] A Mansri; L Tennouga; J Desbrières, *Polym. Bull.*, **2008**, 61, 771-777.

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[20] Y Li, LP Dubin. Polymer-surfactant complexes, In C. A. Herb, & R.K. Prud'homme, Structure and flowin surfactant solutions, ACS symposium series, **1994**, 578, 320–336.
[21] A Avranas; P Iliou, *Colloid and Interface Science J.,* **2003**, 258, 102–109.
[22] MF Winnik; ATS Regismond, *Colloids and Surfaces A*., **1996**, 118, 1–39.
[23] K Kogej; J Skerjanc, *Langmuir.,* **1999**, 15, 4251.