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Rheological Behavior Study of Cationic Surfactant-Polyelectrolyte Complex (AD37/P4VP-DPC) in Aqueous Medium

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Summary: Polyelectrolyte 27% hydrolyzed polyacrylamide-poly(4-vinylpyridine) (AD37-P4VP) complex with cationic surfactant dodecylpyridinium chloride (DPC) interactions in aqueous solution, is investigated by rheological measurements, at 20 °C with a fixed neutralization degree $\alpha = 0.1$. The results show that the interaction of complex (AD37-P4VP) is favored in the presence of the DPC where the electrostatic interactions are dominant. This interaction is governed by electrostatic and hydrophobic interactions. In the presence of salt, it is more cooperative.Three rheological behaviors are determined of this system show a shear thinning behavior, shear thickening for the strong shear rate and a newtonian behavior.Then, we determine the rheological models of the system to different concentration of P4VP in the presence and absence of salt to justify the rheological behavior of the complex.

Keywords: cationic surfactant; neutralization degree; newtonian; polyelectrolyte; rheology; shear thickening; shear thinning

Introduction

The interaction between polymers and surfactants in aqueous solutions has attracted much interest in recent years due to the application of mixed polymer-surfactant systems in various material systems, such as detergents, hair-care products, foams, emulsions, and mineral oil recovery, cosmetic, pharmaceuticals in food and personal care products.[1,2] Polymer–surfactant mixtures are widely used for controlling the colloid stability and rheological properties of complex disperse systems in many practical applications of a charged polymer with a surfactant have been extensively studied.[3,4]

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, drilling fluids, hydraulic fracturing and drag reduction.[5] Poly(4-vinylpyridine) is soluble only in highly polar solvents, reports on the solution properties of P4VP are very limited.[6] Mansri et al.[7] studied the viscosimetric behaviour of the mixture hydrolyzed polyacrylamide–poly(4-vinylpyridine) (AD37–P4VP) in aqueous solution, for a degree of neutralization $\alpha = 1$. The results showed that intermolecular electrostatic association was favoured by increasing the P4VP concentration. Thus, mixtures rich in P4VP were characterized by a substantial decrease in viscosity because of complete (AD37–P4VP) interpolymer complexation, leading to total contraction or collapse of the polymer chains. The greatest reduction in viscosity, because of inter-chain AD37 association, was observed for mixtures poor in P4VP.

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The hydrodynamic and rheological behavior of polyelectrolyte complex (P4VP-AD37) mixture depends on several factors such as polymer concentration, salt, temperature, shear stress, pH of the solution, and the hydrophobicity of the P4VP polymer.[7] In order to gain a more detailed insight into these phenomena, we have carried out rheological measurements on semi-dilute systems (P4VP-AD37) in the presence of the fixed concentration of cationic surfactant DPC at different concentration of P4VP and in the presence and absence of salt. Indeed, at low concentrations, the surfactant binds individually to the polyelectrolyte by electrostatic interaction. Cooperative association occurs at the critical aggregation concentration, CAC, as the concentration is increased, because of hydrophobic interactions between the surfactant tails. This aggregation process leads, occasionally, to a bead-and-necklace type structure in which surfactant aggregates are located along the polyelectrolyte chain.[8]

The change of rheological property of polymer solutions induced by surfactants with the same charge is very important for precise control of the polymers in practical applications.[9]

In a previous paper[10,11] the system (hydrolyzed polyacrylamide, AD37–poly(4-vinylpyridine), P4VP) complex in aqueous solution and in the presence of sodium dodecyl sulphate (SDS) was studied.

In this study, the specific role of a cationic surfactant, the DPC, on the rheological behavior of (AD37–P4VP) complex in aqueous solution at T = 20°C was investigated.

Experimental Part

The cationic poly(4-vinylpyridine) was prepared by radical polymerisation of 4-vinylpyridine in methanol as described elsewhere,[12] using AIBN or Benzoyle peroxyde as initiators in toluene at 60 °C following a described procedure.[13] Its viscosimetric average molar mass is estimated to $3.42.10^4$ g/mol.[7]

Copolymer AD37, based on hydrolyzed acrylamide was provided from Rhone-Poulenc Company. Its content in carboxylate function is 27%, and is determined by ^{13}C NMR and potentiometry. Its average macromolecular is estimated at 5.10^6 g/mol by viscosity.[7]

The surfactant N-dodecyl pyridinium chloride (DPC) was provided by the Aldrich Company. Its molecular mass is 283.5 g/mole. The rheological measurements were performed using a rheometer Brookfield DV-III+ type. This rheometer measure the evolution of the viscosity according to the shear rate.

Results and Discussion

The variation of the dynamic viscosity and the shear stress of the system (AD37-P4VP-DPC) as a function of the shear rate from Brookfield rheometer working speed between (0 to 250 RPM) at T = 20 °C, are presented below.

The interactions between particles polyelectrolyte is determined in a direct way the rheological behavior of the suspension. Thus, the presence of an organic additive in the system will affect the overall behavior regardless of the type of macromolecules interaction particles.[14] In the following paragraphs, we present the effect of adding salt on the viscosity and the shear stress of polymers and cationic surfactants.

The rheological characteristics of this system was investigated at fixed concentration $C_{AD37} = 10^{-3}$ g/ml, and C_{P4VP} ranging from $0,1.10^{-4}$ g/ml to 4.10^{-4} g/ml, DPC concentration ($C_{DPC} = 10^{-3}$ g/ml) in the presence and absence of NaCl (0,1 N).

Figure 1 and Figure 2 shows the flow curves at low and large shear rate. It represents the variation of dynamic viscosity and shear stress of mixture (AD37-P4VP-DPC) according to the shear rate. We note that the viscosity is modified by the presence of DPC in the absence and in the presence of salt (NaCl). We observe that the solution has a shear thinning character (Figure 1 and 2).

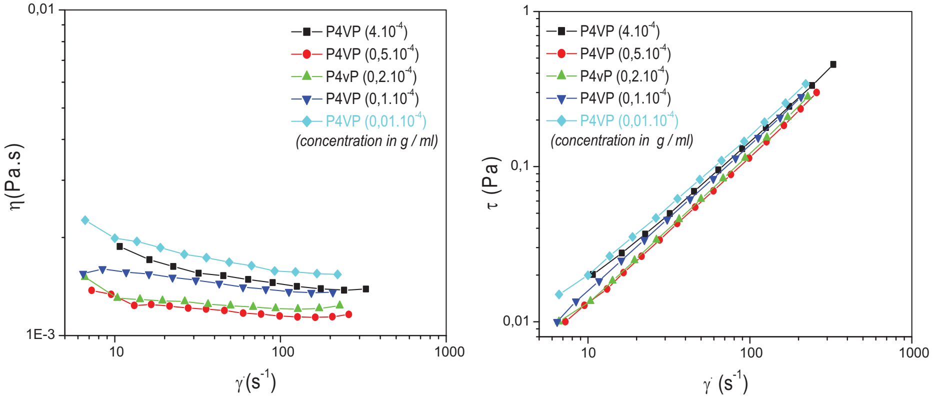

Figure 1.
Variation of dynamic viscosity and shear stress depending on the shear rate of the mixture (AD37-P4VP-DPC), with various concentrations of P4VP and at fixed concentration of $C_{AD37} = 10^{-3}$ g/ml and $C_{DPC} = 10^{-3}$ g/ml at T = 20 °C in the absence of salt.

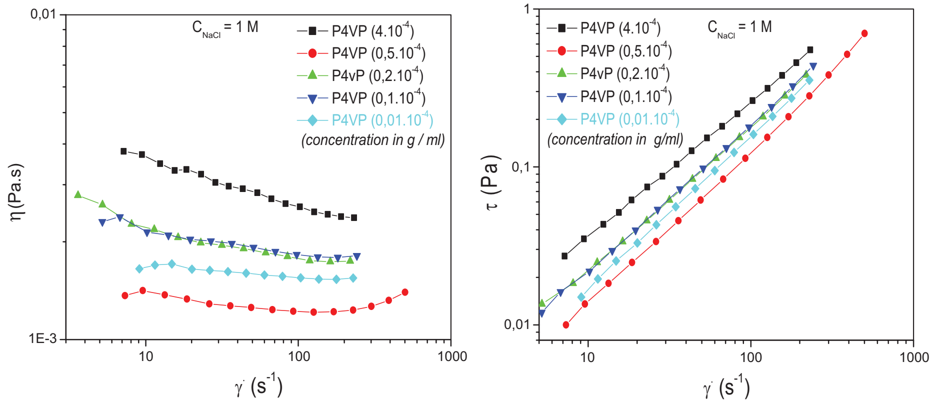

Figure 2.
Variation of dynamic viscosity and shear stress depending on the shear rate of the mixture (AD37-P4VP-DPC), with various concentrations of P4VP and at fixed concentration of $C_{AD37} = 10^{-3}$ g/ml and $C_{DPC} = 10^{-3}$ g/ml at T = 20 °C in the presence of salt.

In the absence of salt and at high shear rate, we find that the viscosity of the solution remains almost constant, which can be considered newtonian. For the Figure 1, we can see that the high viscosity is corresponds to the low concentration of P4VP ($0{,}01.10^{-4}$ g/ml). In presence of salt (Figure 2), we can see that for the concentration of P4VP equal at 4.10^{-4} g/ml the viscosity increases dramatically due to the effect of electrostatic interaction. The variation between the curves becomes important according to the concentration in P4VP. In this case the viscosity of system is strongly modified by the presence of DPC. A shear thickening character is observed for the $C_{P4VP} = 0{,}5.10^{-4}$ g/ml correspond to lower shear rate.

Sites load polyion and hydrophobic interactions increases with increasing concentration of the polymer (P4VP). The addition of salt to the polymer (polyion) (phenomenon screening effect, NaCl screened sites load polyion) and we have a neutral polymer, which increases the hydrophobic interactions that make it more difficult for the flow channels. Thus, the viscosity increases is more important for the high concentration of P4VP (Figure 2). Because, the presence of small amounts of P4VP (a low concentration) and the presence of salt decrease the viscosity of the complex due to weak hydrophobic interaction (screening phenomenon to the neutral polymer), which causes the formation of polymer-surfactant micelles.

The rheological properties of the complex depend primarily on the degree of association of the molecules and thus the polymer concentration regime in which we place ourselves. The polymer concentration is a parameter that largely influences the rheological performance, the molecules of the high molecular weight polymer (P4VP) and form complexes with the AD37 aggregate by hydrogen bonds, electrostatic interaction between charges opposite and entanglement of the polymer chains (hydrophobic interaction).

The AD37 is a polyanion (polyacid) having a flexible pelote conformation, the P4VP is a polycation in the form of a polybase which favored acid-base interaction between the carboxylates' function of the polyanion (AD37) and the nitrogen atom of the pyridine ring.

This behavior is explained by the fact that the carboxyl groups in the molecule AD37 causes good dispersion in water, leading to increased friction between molecules.

The dissociation of the ion Na^+ to AD37 causes the appearance of negative sites along the polymer chain.

We saw in this section that when a polymer is added to a suspension of complex-surfactant. Interactions are favored only the result of a competition between the Van der Waals forces, hydrogen bonds and electrostatic forces of attraction or repulsion between AD37, P4VP and DPC, in the case of mixtures AD37-P4VP-DPC, we can classify the interactions into two major groups:

- An electrostatic interaction between the anionic polymer chains and the existing positive charges on the P4VP.
- An interaction between the negative charges of AD37 and the anionic polymer by the following possibilities:
    - Ion exchange occurs between the carboxyl group of AD37 (COO^-) with the cationic portion of the pyridine ring (acid-base interaction).
    - Hydrogen bonds can form between the P4VP and AD37 of channels.
    - Cation Na^+ and Cl^- may establish electrostatic bridges between the anionic and cationic polyelectrolyte part of AD37-P4VP complex.

We used the algorithms of shear stress according to shear rate to determine a mathematical formalism of the complex (AD37-P4VP-DPC). Which gives the rheological model of the complex which justify the rheological comportment. This model correspond to the model of Herschet-Bulkley ($\tau = \tau_0 + K\gamma^n$), either by the model of Ostwald $\tau = K\gamma^n$, or τ is the shear stress

Table 1.
Rheological characteristics of the different complexes in the absence of salt.

Complex	Shear range	Rheological equation	Rheological model
$C_{P4VP} = 4.10^{-4}$ g/ml In the absence of salt	0 to 328 (s^{-1})	$\tau = 0,0946 + 0,165\gamma^{0,912}$	Model of Herschet-Bulkley $\tau = \tau_0 + K\gamma^n$
$C_{P4VP} = 0,5.10^{-4}$ g/ml In the absence of salt	0 to 258,5 (s^{-1})	$\tau = 0,0094 + 0,128\gamma^{0,9524}$	Model of Herschet-Bulkley $\tau = \tau_0 + K\gamma^n$
$C_{P4VP} = 02.10^{-4}$ g/ml In the absence of salt	0 to 227,9 (s^{-1})	$\tau = 0,0094 + 0,128\gamma^{0,9432}$	Model of Herschet-Bulkley $\tau = \tau_0 + K\gamma^n$
$C_{P4VP} = 0,1.10^{-4}$ g/ml In the absence of salt	0 to 207,3 (s^{-1})	$\tau = 0,0112 + 0,135\gamma^{0,9621}$	Model of Herschet-Bulkley $\tau = \tau_0 + K\gamma^n$
$C_{P4VP} = 0,01.10^{-4}$ g/ml In the absence of salt	0 to 221,5 (s^{-1})	$\tau = 0,157 + 0,168\gamma^{0,8904}$	Model of Herschet-Bulkley $\tau = \tau_0 + K\gamma^n$

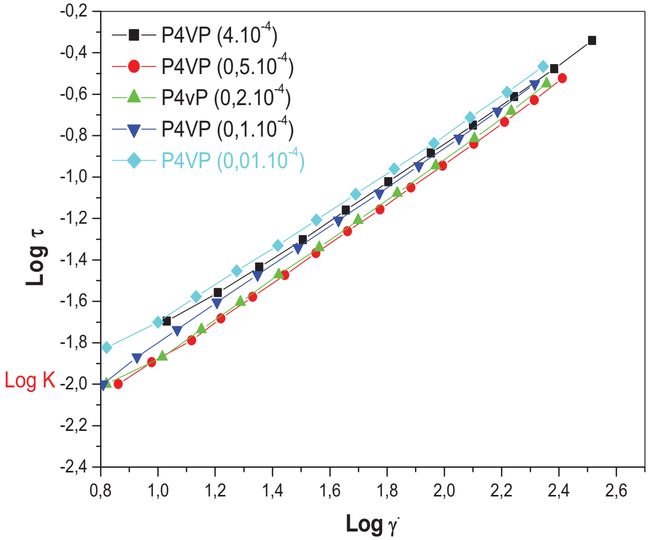

Figure 3.
The logarithmic function of the Stress in relation to shear rate of the mixture (AD37-P4VP-DPC), with various concentrations of P4VP and fixed AD37 concentration $C_{AD37} = 10^{-3}$ g/ml and $C_{DPC} = 10^{-3}$ g/ml at T = 20 °C in the absence of salt.

(Pa), τ_0 the threshold (Pa), $\dot{\gamma}$ shear rate (s^{-1}), n flow indexand K constant fluid ($Pa.s^n$). Presentation by one or other of the models depends on the concentration of P4VP in the presence and absence of salt.

The variation of the logarithmic function of the stress in relation to shear rate of the mixture (AD37-P4VP-DPC) at T = 20 °C in the absence of salt, are presented below (Figure 3).

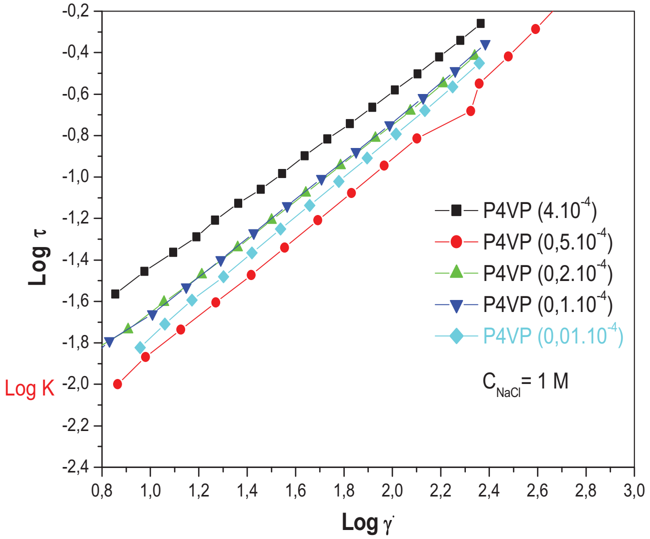

Figure 4.
The logarithmic function of the Stress in relation to shear rate of the mixture (AD37-P4VP-DPC), with various concentrations of P4VP and at fixed concentration in AD37 $C_{AD37} = 10^{-3}$ g/ml and $C_{DPC} = 10^{-3}$ g/ml at T = 20 °C in the presence of salt.

Table 2.
Rheological characteristics of the different complexes in the presence of salt.

Complex	Shear range	Rheological equation	Behaviour and rheological model
$C_{P4VP} = 4.10^{-4}$ g/ml In the presence of salt	0 to 32,08 (s^{-1})	$\tau = 0,0248 + 0,201\gamma^{0,8221}$	*Model of Herschet-Bulkley (Shear thinning)*
	32,08 to 89,73 (s^{-1})	$\tau = 0,0248 + 0,201\gamma^{0,8817}$	
	89,73 to 328 (s^{-1})	$\tau = 0,0248 + 0,201\gamma^{0,8629}$	
$C_{P4VP} = 0,5.10^{-4}$ g/ml In the presence of salt	0 to 500,3 (s^{-1})	$\tau = 0,0085 + 0,201\gamma^{1,005}$	*Model of Herschet-Bulkley (shear thickening)*
	0 to 13,36 (s^{-1})	$\tau = 0,0085 + 0,201\gamma^{1,009}$	
	92,67 to 500,3 (s^{-1})	$\tau = 0,0085 + 0,201\gamma^{0,9571}$	*Model of Herschet-Bulkley (Shear thinning)*
	13,36 to 92,67 (s^{-1})	$\tau = 0,0085 + 0,201\gamma^{1,0788}$	
$C_{P4VP} = 02.10^{-4}$ g/ml In the presence of salt	0 to 218,6 (s^{-1})	$\tau = 0,0146 + 0,129\gamma^{0,886}$	*Model of Herschet-Bulkley (Shear thinning)*
	0 to 22,96 (s^{-1})	$\tau = 0,0146 + 0,201\gamma^{0,8187}$	
	22,96 to 118,8 (s^{-1})	$\tau = 0,0146 + 0,201\gamma^{0,924}$	
$C_{P4VP} = 0,1.10^{-4}$ g/ml In the presence of salt	0 to 242,4 (s^{-1})	$\tau = 0,0146 + 0,201\gamma^{0,924}$	*Model of Herschet-Bulkley (Shear thinning)*
	0 to 36,74 (s^{-1})	$\tau = 0,0146 + 0,201\gamma^{0,924}$	
	36,74 to 242,4 (s^{-1})	$\tau = 0,0146 + 0,201\gamma^{0,924}$	
$C_{P4VP} = 0,01.10^{-4}$ g/ml In the presence of salt	0 to 228,9 (s^{-1})	$\tau = 0,01 + 0,14\gamma^{0,980}$	*Model of Herschet-Bulkley (Shear thinning)*
	0 to 34,56 (s^{-1})	$\tau = 0,01 + 0,14\gamma^{0,987}$	
	34,56 to 228,9 (s^{-1})	$\tau = 0,01 + 0,14\gamma^{0,975}$	

The variation of the logarithmic function of the stress in relation to shear rate of the mixture (AD37-P4VP-DPC) at T = 20 °C in the presence of salt, are presented below (Figure 4).

Conclusion

We came across our work, which includes the study of the rheological behavior of complex (AD37-P4VP-DPC). It shows, the dynamic viscosity which may be affected by the presence and the absence of salt (screening phenomenon), which reduces the electrostatic interactions and repulsions between molecules in the complex.

The results show that the interaction of the system (AD37-P4VP-DPC) is more pronounced for low concentrations of P4VP (0, 01.10^{-4} g/ml), which increases the viscosity of the system. The addition of DPC in the complex (AD37-P4VP) causes a significant increase in the dynamic viscosity of the system with fixing the degree of neutralization ($\alpha = 0.1$). Then, we determine the rheological models of the system to different concentration of P4VP in the presence and absence of salt to justify the rheological behavior of the complex.

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