

## Complexation behavior of polyelectrolyte/polyelectrolyte at weak neutralization degree: Study by several techniques

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### Abstract

The complexation of hydrolyzed polyacrylamide (AD37) and poly(4-vinylpyridine) (P4VP) in aqueous solution at 25 °C was studied by viscosity, conductivity and potentiometry measurements. The result shows, that intermolecular electrostatic association are favored by increasing the P4VP concentration. Thus, mixtures rich in P4VP are characterized by a high decrease in the viscosity due to interpolymer complete complexation AD37-P4VP, leading to the totally contraction or collapse of the polymer chains. So, strongest reduced viscosities, due to the inter-chain AD37 associations, are observed for the mixtures poor in P4VP. Potentiometric, viscometric and conductometric measurements reveal that the complexation of the AD37 with the P4VP is insured by acid–base interaction between the carboxylate function and the partially hydrolyzed pyridinic nitrogen atoms.

**Keywords:** *association, polyelectrolyte, polyelectrolyte complexes, neutralization degree.*

### 1. Introduction

Polyelectrolytes are charged molecules consisting of ionizable groups, which release counterions when desolating in polar solvents such as water. In the recent years, polyelectrolytes have been extensively studied due to a number of potential applications in many industrial processes, such as filtration, water treatment, papermaking, food manufacturing, and mineral extraction [1–6]. In those processes, they are widely used as thickeners, emulsifiers, flocculants, and conditioners [7]. Electrostatic interactions between charges lead to the rich behavior of polyelectrolyte solutions qualitatively different from those of uncharged polymers [8–10]. Interactions between oppositely charged polyelectrolytes have attracted a considerable interest because of the possibilities of applications of their products-polyelectrolyte complexes (PECs) [11-14]. These complexes are stabilized by either electrostatic interactions between a polyanion and a polycation or by hydrogen bond formation (polyacid–polybase). Polyelectrolyte complexes'' (PECs) is a very broad term that generally describes polymer networks formed by the electrostatic attraction of oppositely charged polyions [15]. This complex formation is guided by polymer parameters (i.e.charge density, molar

mass, concentration, chemical nature and ratio) and by environmental conditions such as pH, ionic strength, and ion type [16]. 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 [17]. Polyvinylpyridines have interesting chemical properties thanks to the nitrogen atom of the aromatic nucleus. Indeed, these copolymers are obtained by radical polymerization of vinylpyridines, but since the P4VP is soluble only in highly polar solvents, reports on the solution properties of P4VP are very limited [18]. In this paper, our study focuses on the complexation between hydrolyzed polyacrylamide (AD37) and poly(4-vinylpyridine) (P4VP), using the conductivity, the potentiometry and the viscosity techniques at  $T=25^{\circ}\text{C}$ . It should be noticed that we will restrict our efforts to the case when the neutralization degree is  $\alpha=0.1$ . The parameter  $\alpha$  represents the quantity of protons  $\text{H}^+$  added compared to the concentration of the P4VP.

## 2. Experimental part

### 2.1. Products

Copolymer AD37 based on hydrolyzed acrylamide was provided from Rhône-Poulenc Company (France). Its content in carboxylate functions is 27 %, determined by  $^{13}\text{C}$  NMR and potentiometry. Its molar mass is estimated to  $5.10^6 \text{ g mol}^{-1}$  by light scattering technique [17, 19]). P4VP polymer was synthesized by radical polymerization. In its neutral form, it is not soluble in water at neutral pH. Nevertheless, it's highly polar character induces good solubility in polar organic solvents like DMSO, DMF, methanol or ethanol. Its molar mass is estimated at  $4.10^4 \text{ g mol}^{-1}$ , by light scattering technique.

### 2.2. Apparatus

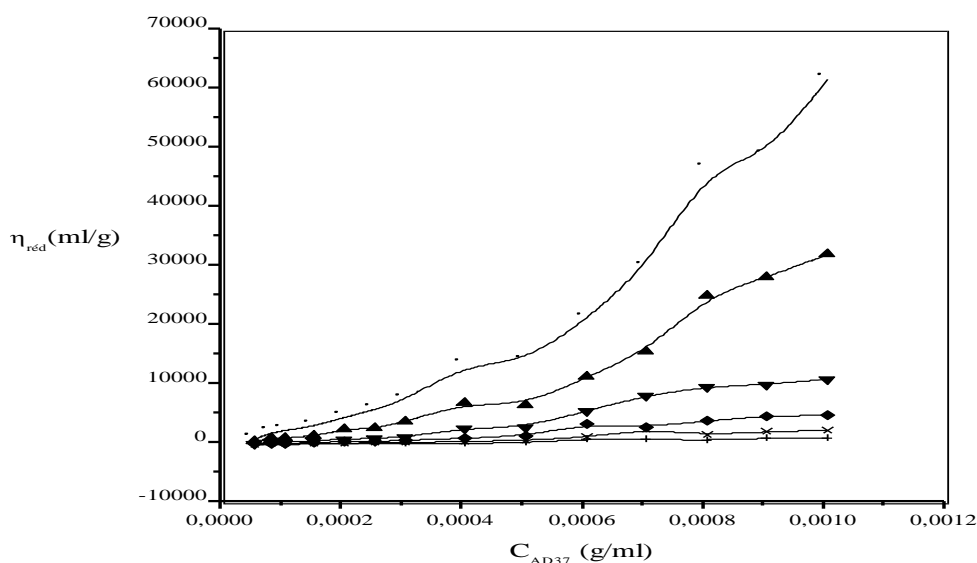
An Ubbelohde viscometer was used to measure the viscosities of polymer solutions. The viscometer was placed in a thermostated bath at appropriate temperature, controlled within the range of  $\pm 0.1^{\circ}\text{C}$ . Our conductimetric measurements were made using a conductivity meter CDM 210 (Radiometer, Meter Lab). The solutions studied are contained in a glass cell thermostated double-walled ( $25 \pm 0.1$ )  $^{\circ}\text{C}$  using a heating circulator.

## 3. Results and discussion

### 3.1. Viscometric study of the mixture AD37-P4VP- $\text{H}_2\text{O}$

The neutralization degree  $\alpha$  represents the quantity of protons  $\text{H}^+$  added compared to the concentration of the P4VP. Figure 1 shows the variation of reduced viscosity of mixture AD37-P4VP in aqueous solution and in the presence of hydrochloric acid HCl in decimolar quantity compared to that of the P4VP. This system can be regarded as ternary AD37-P4VP-  $\text{H}_2\text{O}$  with a fixed neutralization degree  $\alpha=0.1$ . We notice an increasing variation of the reduced viscosity according to the concentration in AD37. The viscosity of the mixture strongly increases when the concentration in P4VP decreases. Thus, for a mixture of strong concentration in AD37 ( $10^{-3}\text{g/ml}$ ) and of weak concentration in P4VP ( $10^{-5}\text{g/ml}$ ), we record a value of the reduced viscosity about

61942 ml/g. For an excess of forty times of P4VP ( $4 \times 10^{-4}$  g/ml), reduced viscosity passes from 61942 ml/g to 1140 ml/g (concentration in P4VP =  $10^{-5}$  g/ml), that is to say a fall of 54 times.



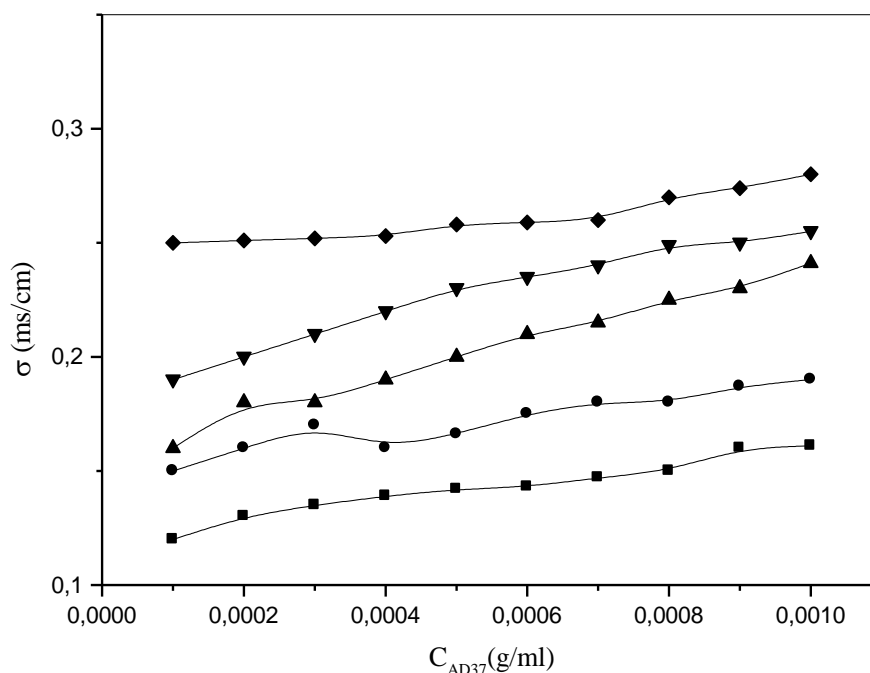
**Figure 1:** Variation of the reduced viscosity of the ternary mixture (AD37-P4VP-H<sub>2</sub>O) according to  $C_{AD37}$  for  $\alpha=0.1$  and at various concentrations of P4VP (g/ml):  $10^{-5}$  (●);  $2.10^{-5}$  (▲);  $5.10^{-5}$  (▼);  $10^{-4}$  (◆);  $2.10^{-4}$  (×);  $4.10^{-4}$  (+).

For each fixed concentration in P4VP, viscosity increases in an unusual way, according to the concentration in AD37. This phenomenon cannot be explained only by the phenomenon of association which will be intra and/or inter-chains, occurring following the changes of structures of acid functions COOH of the AD37. Indeed, the P4VP 10% hydrolyzed by HCl, form a complex AD37-P4VP. The presence of sequences of charged sites with opposed signs creates zones of local intense electrostatic fields and reinforces attractions polyacid-polybase, therefore of complexation. When the concentrations in P4VP exceed  $10^{-4}$  g/ml, the complexation polymer-polymer AD37-P4VP involves the collapse of the polymeric chains, resulting in a fall of reduced viscosity.

### 3.2. Conductimetric study of the (AD37-P4VP) system

Figure 2 shows the change of the conductivity of the mixture as a function of the AD37 concentration, for varying concentrations of P4VP and in the presence of HCl in an amount decimolar compared to that of the P4VP. For each concentration of P4VP, the conductivity increasing as a function of the concentration of AD37 du to the increase rate of negative charges segments of AD37 with its concentration. Thus, we observe for the high concentration of P4VP a total electrostatic association between the negative chains of AD37 and the positive chains of the

P4VP, leading to a total liberation of the  $H^+$  ions. Thus, we observe a great increasing of the conductivity.



**Figure 2:** Variation of the conductivity of the system (AD37-P4VP) at  $T = 25\text{ }^{\circ}\text{C}$  depending on the AD37 concentration for  $\alpha = 0.1$  and at various concentrations of P4VP (g/ml):  
 (■)  $10^{-5}$ ; (●)  $5 \cdot 10^{-5}$ ; (▲)  $10^{-4}$ ; (▼)  $2 \cdot 10^{-4}$ ; (◆)  $4 \cdot 10^{-4}$

Figure 2 shows the change of the conductivity of the mixture as a function of the AD37 concentration, for varying concentrations of P4VP and in the presence of HCl in an amount decimolar compared to that of the P4VP. For each concentration of P4VP, the conductivity increasing as a function of the concentration of AD37 due to the increase rate of negative charges segments of AD37 with its concentration. Thus, we observe for the high concentration of P4VP a total electrostatic association between the negative chains of AD37 and the positive chains of the P4VP, leading to a total liberation of the  $H^+$  ions. Thus, we observe a great increasing of the conductivity.

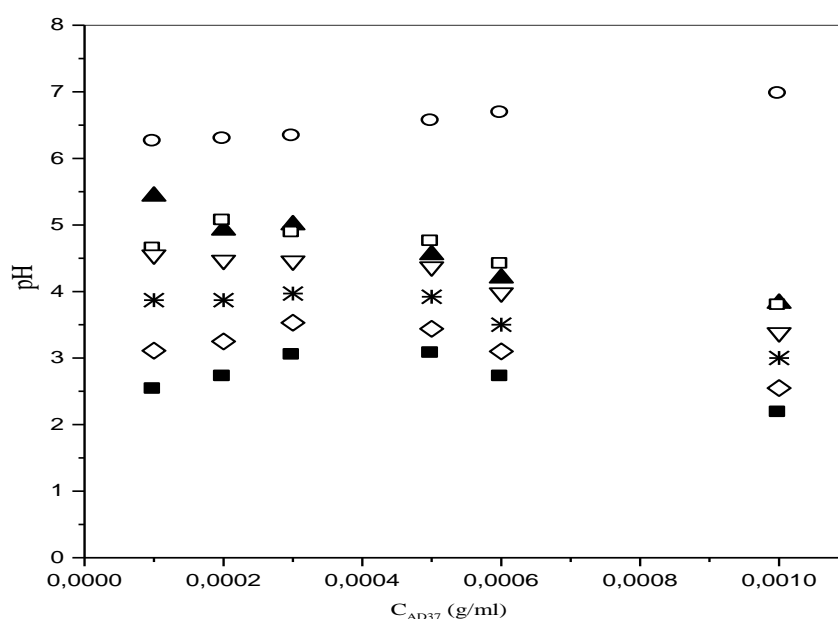
### 3.3. Potentiometric study of the (AD37-P4VP) system

On the figure 3, the pH of AD37 alone increase according to its concentration. For the mixture, we observe two fields for all P4VP concentrations:

- i- For the  $C_{AD37} \leq 3 \cdot 10^{-4}$  g/ml; a weak increase in pH is due to the inter-chain association phenomenon between AD37 and P4VP copolymers.
- ii- When the  $C_{AD37}$  exceed  $3 \cdot 10^{-4}$  g/ml; a weak decrease in pH of the system is due to the intra and intermolecular complete complexation AD37-P4VP, leading to the totally contraction or collapse of the copolymer chains.

These pH curves show that the AD37 copolymer conformation is depending on the ratio of the P4VP copolymer. In fact, for the very weak quantities of the P4VP, we observe a progressive decreasing of the pH as a function of AD37 concentration. Oppositely, for the high concentrations of the P4VP, we observe a progressive increasing of the pH for the weak AD37 concentrations, showing a direct effect of the P4VP copolymer on the pH.

This phenomenon reach a maximum at AD37 concentration about  $C_{AD37} = 3.10^{-4}$  g/ml, from which the number of AD37 chains reach a critical limit of power to break the solid structure formed by the P4VP chains. At the concentration  $C_{P4VP} = 4.10^{-4}$  g/ml, there is no doubt that we observe a total electrostatic association of the negative chains of AD37 with the positive chains of the P4VP, leading to a total liberation of the  $H^+$  ions. Thus, we observe both significative pH decreasing, a spontaneous decreasing of the viscosity and a great increasing of the conductivity.



**Figure 3:** Variation of the pH of the ternary mixture (AD37-P4VP- $H_2O$ ) according to  $C_{AD37}$  for  $\alpha=0.1$  and at various poly(4-vinylpyridine) concentrations : [P4VP] (g/ml):  $10^{-5}$  ( $\blacktriangledown$ );  $2.10^{-5}$  ( $\square$ ) ;  $5.10^{-5}$  ( $\nabla$ );  $10^{-4}$  ( $*$ );  $2.10^{-4}$  ( $\diamond$ );  $4.10^{-4}$  ( $\blacksquare$ ); ( $\circ$ ) AD37 alone.

#### 4. Conclusion

The present study confirms that the hydrolyzed polyacrylamide and poly(4-vinylpyridine) forms a reticule network, in aqueous solution. The reaction follows a complexation of (AD37) polyanions with (P4VP) polycations. This complexation reaction generates hydrophilic associated (AD37/P4VP) segments of the same length than that of the P4VP chains. The ratio of the generated associated (AD37/P4VP) segments is directly linked to the P4VP ratio in the system. Thus, the present system will contain two segment types. The first is hydrophilic and the second is more

hydrophobic with non hydrolyzed carboxylic acid function. These last copolymer complex segments generally join between them and form big size chains.

Intermolecular electrostatic associations are favored by increasing the P4VP concentration. Thus, mixtures rich in P4VP are characterized by a high decrease in the viscosity due to interpolymer complete complexation AD37-P4VP, leading to the totally contraction or collapse of the polymer chains. So, strongest reduced viscosities, due to the inter-chain AD37 associations, are observed for the mixtures poor in P4VP.

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