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Neutralization degree effect on viscosimetric behaviour of hydrolyzed polyacrylamide-poly(4-vinylpyridine) [AD37-P4VP] mixture in aqueous solution

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Abstract

In the present work, we describe the dependence of the 27 % hydrolyzed polyacrylamide [AD37]-poly(4-vinylpyridine) [P4VP] mixture reduced viscosity as a function of the neutralization degree of P4VP polymer, in aqueous solutions at 25°C. Measurements are performed using the viscosimetry technique.

Viscosity results showed that the polymer chains expanded at low neutralization degrees ($\alpha<1$). But, collapse is observed at high neutralization degrees of amine groups ($\alpha>1$). We note that the viscosity get a maximum at $\alpha \approx 0.86$

Introduction

Although the exceptional behaviour of polyelectrolytes in solution is a matter of considerable scientific and technological interest, physico-chemical properties of mixtures still need further understanding [1].

The concentration dependence of the reduced viscosity of salt-free polyelectrolyte solutions exhibits an unusual behaviour because it increases with decreasing polyelectrolyte concentration [2, 3]. Qualitatively, this was explained by a coil-to-rod transition of the polyions upon dilution due to the increasing electrostatic interactions along the chains with decreasing ionic strength. Careful but still controversial investigations of the dilute solution behaviour [4-6] reveal that the rise of the reduced viscosity is always followed by a maximum with a subsequent steep decrease at the lowest concentrations. The concentration where the maximum is observed is independent of molecular weight and depends only on the ratio C_{pe}/C_s (where C_{pe} and C_s are the polyelectrolyte and salt concentrations respectively). Rabin [4] derived a theoretical expression for the viscosity of such solutions, assuming that the hydrodynamics of low ionic strength polyelectrolyte solutions is dominated by the electrostatic repulsion between the polyions.

Partially hydrolysed polyacrylamides are used in the processes of secondary oil recovery processes, as thickening agent, to lower the mobility of the aqueous phase compared to the oily phase. One can thus increase the production of a well by recovering part of inaccessible oil by the traditional processes [7]. Such polymers are also used in other industrial processes such as flocculation, etc.... The study of their properties was the objects of many works [8] since they constitute interesting models of flexible polyelectrolytes with variable charge density. These partially hydrolyzed polyacrylamides have the chemical structure presented on figure 1.

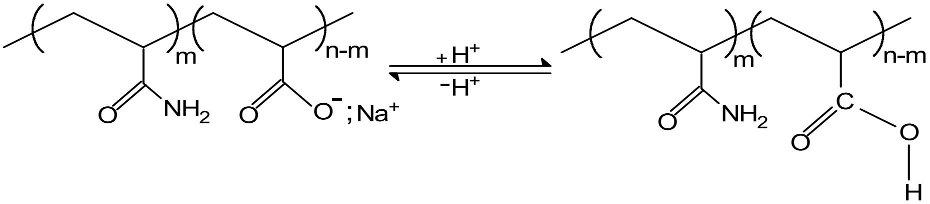

Figure 1: Chemical structure of the partially hydrolyzed polyacrylamide in presence and absence of protons H+.

Polyvinylpyridines have interesting chemical properties thanks to the nitrogen atom of the aromatic nucleus. Indeed, these copolymers are obtained by radical polymerization of vinylpyridines [9]. They have many applications in non-polluting paintings using water for solvent, in food industry and the fields of biology, etc...[9].

Poly(4-vinylpyridine) is neutral at pH≥7 and hence is insoluble in pure water. In the presence of protons (in acidic medium), it becomes cationic and water soluble (figure 2). The two polyelectrolytes forming this system were the object each one of several physicochemical studies. Their potentiometric (sensitivity with respect to the protons), viscosity, associative and conformational behaviours are well-known [7-9].

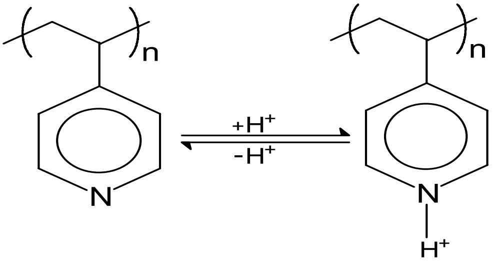

Figure 2: Chemical structure of poly(4-vinylpyridine) in presence and absence of protons H^+.

Polyelectrolyte complex formation between polyanions and polycations can take place via the attraction forces, such as Coulomb interactions and hydrogen bonds, etc...[10]. Crescenzi et al. [11, 12] carried out a calorimetric study of the ionization of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) and found that while the enthalpy of ionization, ΔH^i, was a smooth function of the ionization degree, α, for PAA, the PMA plot exhibited an endothermic peak (which became larger at higher temperatures) in the region in which viscosity and potentiometric titration indicated the transition from the contracted to the expanded form.

A study of the potentiometric titration and viscosity behaviour of PAA in methanol was reported from Mandel's laboratory [13]. It was found that the change of both pK_a and reduced viscosity with the neutralization degree was strikingly different depending on whether $LiOCH_3$ or $NaOCH_3$ was used as titrating agent. Both produced a collapse of the polyion at a relatively low degree of neutralization, but this collapse was much sharper in the case of $NaOCH_3$, leading to more compact particles.

The contact between these two polyelectrolytes, under these conditions, allow to follow the various types of interactions of both polyions according to their relative concentrations and neutralization degree α of poly(4-vinylpyridine).

Experimental

Instruments

Viscosity was measured with a capillary standard Ubbelohde viscometer at a constant temperature of 25°C ± 0.1°C. Reduced viscosity ($\eta_{red} = \eta_{sp}/c$) was calculated at zero shear rate as the ratio of specific viscosity (where η and η_0 are viscosities of the polymer solution at the desired concentration and solvent respectively) and polymer concentration, c.

The weight-average molar mass was obtained using light scattering spectrophotometer from Brice-Phenix.

Materials

Copolymer AD37 based on hydrolyzed acrylamide was provided from Rhône-Poulenc Company (France). Its content in carboxylate function is $\tau = 0.27$ and is determined by ^{13}C NMR and potentiometry. Its weight-average molar mass is estimated to $5\text{x}10^6$ g/mole by light scattering technique [7, 14].

Poly(4-vinylpyridine) polymer was synthesized by radical polymerization [9]. 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 weight-average molar mass is estimated at $4\text{x}10^4$ g/mole, by light scattering technique.

The following solvents and products (sodium chloride NaCl, hydrochloric acid HCl 37.5% and methanol), from Prolabo, were used without any later purification.

Preparation of AD37 polyelectrolyte solution

In order to obtain a concentration of 10^{-2}g/ml of AD37, a quantity of 10g was dissolved in 1000ml distilled water using a graduated flask. Magnetic stirring during 48 hours, at ambient temperature allows obtaining solution. Let us note that a slight heating of the solution at the beginning of agitation will better stimulate the polymer solubility in water. The solution obtained is then filtered using a usual filter paper.

Preparation of poly(4-vinylpyridine) solution

A 1.13g P4VP is introduced into a graduated flask of 25ml. A volume of methanol equal to 12.5ml is added to polymer. Agitation is engaged and a quantity of HCl is added in order to adjust the ionic charge factor, α. Solution was filled to 25ml with water and stirred during 48 hours at ambient temperature. The solution was then filtered using an usual filter paper.

Dilutions

The solutions of various concentrations were prepared by dilutions from AD37 and P4VP stock solutions. They are stirred during at least two hours to homogenize them before using them in viscosity measurements.

Results and Discussions

The neutralization degree α represents the molar quantity of added protons H^+ compared to the monomol P4VP polymer concentration.

Figures 3, 4 and 5 show plots of reduced viscosities variation of the ternary system (AD37-P4VP-water) as a function of the neutralization degree, α, for fixed P4VP and various AD37 concentrations. We note that the reduced viscosity variations are similar for all P4VP concentration. In the same time, an important opposite effect was observed for the two polymers. The P4VP lead to decrease the viscosity system, however the AD37 increases the viscosity.

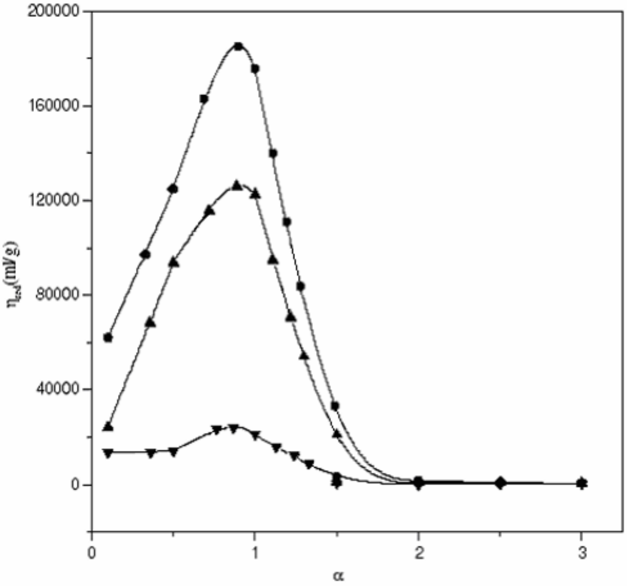

Figure 3: Variation of the reduced viscosity of the ternary mixture (AD37-P4VP-H_2O) according to neutralization degree for C_{P4VP}=10^{-5}g/ml for various AD37 concentrations: [AD37](g/ml) = 10^{-3} (•); $7x10^{-4}$ (▲); $4x10^{-4}$ (▼).

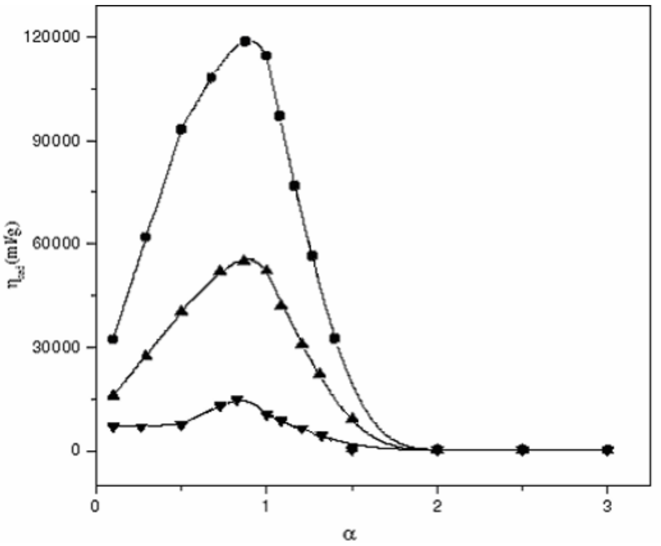

Figure 4: Variation of the reduced viscosity of the ternary mixture (AD37-P4VP-H_2O) according to neutralization degree for C_{P4VP}=2x10^{-5}g/ml for various AD37 concentrations: [AD37](g/ml) = 10^{-3} (•); 7x10^{-4} (▲); 4x10^{-4} (▼).

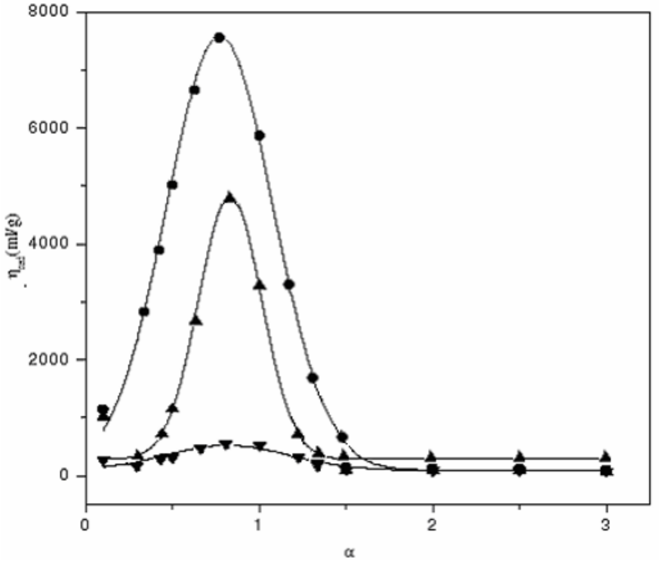

Figure 5: Variation of the reduced viscosity of the ternary mixture (AD37-P4VP-H_2O) according to neutralization degree for C_{P4VP}=4x10^{-4}g/ml for various AD37 concentrations: [AD37] (g/ml) = 10^{-3} (•); 7x10^{-4} (▲); 4x10^{-4} (▼).

We distinguish three different areas according to α values:

$0 < \alpha < 1$

The reduced viscosity increases rapidly by initial acid addition until a maximum was reached. This maximum appears before the addition of one acid equivalent to the polymer solution. This variation increases with the increase in AD37 concentration. Indeed, the great values of viscosities are recorded for the weak concentrations in P4VP. Thus, the two polymers are simultaneously responsible for the increase and decrease in the reduced viscosity of the system. These viscosity increases are interpreted by the association's effect for the AD37 chains. Viscosity reaches a maximum for $\alpha = 0.86$ whatever the polymer concentrations. Fuoss et al. [15] showed that the reduced viscosity of the P4VP solutions in the water-methanol mixture decreases at $\alpha = 1$. Herbert et al. [16] showed that the reduced viscosity of the solutions of PAA in methanol decreases at $\alpha = 0.25$. Cohen et al., Eisenberg et al. [4–6], in their investigations of the dilute solution behaviour show that the rise of the reduced viscosity is always followed by a maximum with a subsequent steep decrease at the lowest concentrations.

Considering all these previous system behaviours, we observe that our system has similar variations, but with a specific maximum and very important viscosity variations, linked to the P4VP concentrations (see figures 3, 4 and 5). This polymer complex system has a similar behaviour like one simple polyelectrolyte water solution.

$1 < \alpha < 1.5$

The viscosity decrease was accompanied by the appearance of a disorder, showing the beginning of precipitation of the AD37 by the protons H^+. This comes down to tell that the addition of HCl great quantities lead to decrease the reduced viscosity system. AD37 becomes less charged.

$1.5 < \alpha < 3$

Reduced viscosities stabilize and take a pace linear and constant according to the neutralization degree α and this whatever the polymer concentration (AD37, P4VP). The viscosity values are very weak and incomparable with the measured values for the first area ($0<\alpha<1$). Indeed, in this area, there is a quite marked phenomenon of precipitation which leads to decrease the viscosity of the system, where the chains of the P4VP leave completely the chains of AD37. Thus, formation of monomeric carboxylic units along the chains of AD37 which are insoluble in water (hydrophobic) was considered. The other sites of the P4VP are hydrophilic and "dissolve" completely in the aqueous medium.

Mechanism of the complexation polyanion-polycation

The complexation of the AD37 with the P4VP is insured by acid-base interaction between the carboxylate function and the pyridinic nitrogen atom. This reaction depends on the quantity of proton present in the medium.

Addition of protons to this AD37-P4VP polymers mixture causes, at the same time, the protonation of the pyridinic functions and the neutralization of the carboxylate ones (COO^-) presents on the AD37 chains, to transform them into pyridinium and carboxylic acid functions, respectively. We note that the hydrogen bond established between the nitrogen atom and the carboxylic acid function is of very strong nature since it allows the mutual neutralization of the two antagonistic functions (acid pyridinium and basic carboxylate one). This hydrogen bond constitutes a true bridge between the two polymers AD37 and P4VP chains, which join according to their number.

These polymer segments (complex) generally join between them. We thus have a system equivalent to a "poly-block" copolymer.

Conclusion

The follow-up of the rheological behaviour of this system by viscosimetry showed that the reduced viscosity grows quickly with initial addition of acid following the effects of associations and the chains expansions of AD37, until reaching a maximum at a neutralization degree, α, equal to 0.86. Beyond this maximum, reduced viscosity decreases slowly to reach a value dependent on the total polymer concentration. Then, it is stabilized and takes a linear type variation, where the chains of the P4VP separate completely from the chains of AD37. Indeed, the chains of P4VP reach their maximum load factor and become completely water soluble. COO^- carboxylate groups are transformed into COOH form by action of H^+ ions, when α increases. This causes separation between the two acid forms COOH and N^+, leading to a disappearance in AD37-P4VP interaction.

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References

[1] Forster S, Schmidt. M and Antonietti. M., *Polymer* **1990**, 31, 781.

[2] Fuoss, R. M., *J. Polymer Sci.* **1948**, 3, 603.

[3] Fuoss, R M., *J. Polymer Sci.* **1949**, 4, 96.

[4] Cohen. J, Priel. Z and Rabin .Y., *J. Chem. Phys.* **1988,** 88, 7111.

[5] Eisenberg. H and Pouyet. J., *J. Polymer Sci.* **1954**, 13, 85.

[6] Cohen. J and Priel. Z., *Macromolecules* **1989**, 22, 2356.

[7] a- N. Truong Dinh. PhD thesis, **1984,** Strasbourg, France**.**
b- N. D. Truong, J.C. Galin, J. François and Q.T. Pham, *Polymer*, **1986,** 27, 467.
c- N. D. Truong, J.C. Galin, J. François and Q.T. Pham, *Polym. Commun.,* **1984,** 25, 208.
d- R. Rabhari. PhD thesis, **1988,** Strasbourg, France**.**
e- R. Rabhari and J. François, *Polymer,* **1988,** 29, 851.
f- R. Rabhari and J. François, *Polymer,* **1992,** 33, 1449.
g- R. Rabhari and J. François, *Polymer,* **1988,** 29, 845.
h- E. Choukchou, Master Diploma, **1999,** Tlemcen, Algeria**.**

[8] a- Y. Feng. *Polym. J.,* **2005**, 46, 9283.
b- M. Mandel and T. Odijk, *Ann. Rev. Phys. Chem.* **1984,** 35, 75.

[9] a- E. Choukchou, I. Benabadji, J. François and A. Mansri, *Eur. Polym. J.*, **2003,** 39(2), 297-303.
b- A. Mansri, L. Tennouga and J. Desbrières, *Eur. Polym. J.* **2007**, 43, 540-549.

[10] a- J. Desbrières and M. Rinaudo. *Eur. Polym. J.,* **1981,** 17. 1265-1269.
b- E. Tsuchida and Abe. K., *Adv. Polym. Sci.* **1982**. *45*. 1.

[11] Crescenzi V., Quadrifoglio F. and Delben F., *J. Polym. Sci., Part. A-2* **1972**, 10, 357.

[12] Delben F., Crescenzi V. and Quadrifoglio F., *Eur. Polym. J.* **1972**, 8, 933.

[13] Klooster N. T. M., Van der Touw F. and Mandel M., *Macromolecules,* **1984**, 17, 2070.

[14] G. Medjahdi. PhD thesis, **1989,** Strasbourg, France.

[15] R. M. Fuoss and W. N. Maclay, *Journal of Polym. Sci.*, **1951,** 3, 305.

[16] Herbert. M. Yongcai. W. *Macromolecules,* 1**987,** 20. 194-195.