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Potentiometry and conductimetry characterizations of poly (4-vinylpyridine) homopolymer in dilute water/methanol solutions

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ABSTRACT

A set of poly(4-vinylpyridine) were synthesized by free radical polymeriza tion and characterized by ^{1}HNMR spectroscopy. The weight average molar mass were determined by light scattering and by viscosimetry. This work describes the effects of the molecular weight and the concentration on the interaction of poly(4-vinylpyridine) [P4VP] with proton H^+ at 25°C, until total neutralization range (0-1). Interactions are followed by potentiometry and conductimetry techniques, in water/methanol mixture. We have considered three P4VP samples: P4VP1, P4VP2 and P4VP3 with respective molecular weights: 6×10^4, 18.45×10^4, 44×10^4 g/mol, and for two different concentrations: 1.6×10^{-4} to 7.98×10^{-3} monomol/l. The phase diagrams were established and reveal ranges of concentration of polymer and solvent composition where phase separation occurs. It sorts that the solubility domain of P4VP is limited and critical point is observed: 64 % (v/v) for water/methanol mixture and 4 mg/ml of polymer concentration. The solubility is independent of the molecular weight. Many experimental studies have been performed at a particular concentration and particular molecular weight and the variation of pKa with polymer concentration and molecular weight was generally neglected[1-4]. However, we show in this paper the variation of both pKa and pK_0 according to the concentration and the P4VP molecular weight. The P4VP-H^+ is a low charged poly electrolyte where the hydrogen bonds are responsible for the compact conformation. The pK_0 depends on both the concentration and the polyelectrolyte conformation. The critical ionization degree is 0.2 in 50/50 v/v water/methanol mixture. For higher neutralization values, no further changes of the structure and the conformation, were observed. It was concluded that an equilibrium exists between N and N^+ in P4VP/HCl system in 50 % water/methanol solution.

KEYWORDS

INTRODUCTION

Polyelectrolyte solutions are known with their different properties from those of both electrolytes and neutral polymers. The characteristic properties of polyelectrolyte solutions have been accounted for by the strong electrostatic potential produced by a large number of charges on a polymer chain[5-6].

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The poly(4-vinylpyridine) [P4VP] is a weak polybase, which is obtained by radical polymerization. In its neutral form, it is not soluble in water at neutral pH. P4VP is only soluble in very polar solvents[1-2] or in the aqueous acid[4].

In this paper, the P4VP solution properties, using hydrochloric acid as protonating agent, were investigated. Nevertheless, its highly polar character induces good solubility in polar organic solvents like methanol or ethanol. The P4VP critical concentration Cp* (4 mg/ml), at phase separation, is expected to be independent on the P4VP molecular weight.

Thus, the water percentage influence on the P4VP solubility in water/methanol mixtures is followed for several molecular weights (6×10^4, 18.45×10^4, 44×10^4 g/mol). The ion-polyion interactions were studied by potentiometry and conductimetry titrations.

A number of papers have dealt with ionic equilibrium of polybases, such as poly(4-vinylpyridine)[2-3,7-8]. The litterature data[3,7-11] show that electrostatic interactions in polyelectrolytes generally affect macromolecule properties in two ways:

-First, they decrease the degree of ionization compared to the monomer analogues.

-Second, they change the conformation free energies, and consequently, change the distribution function of the conformation set for the macromolecule. Previous papers[3,7] have reported that the value of intrinsic pK_0 of pyridine unit in P4VP is appreciably less than the value of pKa for the analogue monomer 4-ethylpyridine (Etpy) in water and ethanol/water solutions. But, the variation of Ka with the polymer concentration and molecular weight was generally neglected. The purpose of the present work is to clarify these phenomena caused by the binding of protons in water/methanol mixtures, at several P4VP concentrations (1.6×10^{-4} to 7.98×10^{-3} monomol/l) and for different molecular weights.

In this way, we have established a phase separation diagram as a function of water percentage. Different polymer behaviour in water/methanol, are examined by means of pH titration of the P4VP. The apparent dissociation constant pKa, which is a sensitive function of the electrostatic potential[4,12-13] of the protonated polymers, is estimated with changing the protonation degree and the corresponding pH values. The

dissociation constants of pyridine residue of polymers in the absence and presence of electrostatic interaction (pK_0) are lower than for the monomer analogue 4-ethylpyrine and depend on molecular weight and concentration of P4VP.

The critical protonation degree (0.2) is evaluated by using two different techniques, conductimetry and potentiometry, which give two near and similar values.

2. EXPERIMENTAL

2.1. Apparatus

Viscosimetric measurements

The viscosity of P4VP was measured with an Ubbelohde viscosimeter at $(25 \pm 0.1)°C$ in ethanol solution.

Light scattering

Brice-Phenix Light Scattering Photometer was used.

Nuclear magnetic resonance spectra

^{1}H NMR spectra were recorded on Bruker 400 MHz spectrometer at 25°C in deuterated chloroform ($CDCl_3$) as solvent.

Conductimetric titrations

Conductance measurements were done with "Conductivity Meter CDM210" (constant=$1 cm^{-1}$) in water/methanol using a double platinium electrode. The equilibrium was reached after approximately 15 mn. The vessel was thermostated at 25°C.

pH metric titrations

pH metric titrations were performed in a thermostated vessel at 25°C using a "*Denver Instrument*" model 225, equipped with a Schott combined electrode. The system was standardized with buffers solutions at pH 4.01 and 7.02. In the high pH range, the stabilization of the pH solutions of P4VP needed a few minutes; thus, further addition of the titrant was delayed until a constant value of pH.

2.2. Preparation and characterization of the linear P4VP

P4VP was prepared by radical polymerization of 4-vinylpyridine (65°C at 15 mmHg, n_D^{20}=1.5520, using AIBN as initiator, in toluene at 60°C following

described procedures[14-15].

P4VP samples were fractionated by successive dissolution-precipitation steps in the following solvents: chloroform/hexane or methanol/ethylacetate. Three main fractions (P4VP1; P4VP2 and P4VP3) were obtained in this way with molecular weights: 6×10^4, 18.45×10^4, 44×10^4 g/mol. Molecular weights were calculated by Mark-Houwink law (1) proposed for the P4VP/ethanol system at 25°C[16].

$$[\eta] = 6.08 \times 10^{-4} \, Mw^{0.61} \qquad (1)$$

Where $[\eta]$ is the intrinsic viscosity and Mw is the molecular weight.

^{1}HNMR spectra for both samples of P4VP (CDCl$_3$, δ ppm) present following signals: (8.31; N-C-H); (6.37; N-C-C-H); (1.51–2.37; -CH$_2$-CH-).

2.3. Preparation of solutions

As recovered from the polymerization (ie., in basic form) P4VP is not soluble in water. Thus, the sample is first dissolved in methanol. The solutions were prepared at least 24 h before experiments, and homogenized at 25°C by direct dissolution in methanol. In the case, 100% water, the P4VP was dissolved in minimum of chloride hydrogen. The solubilisation was determined in phase diagrams.

2.4 Solubilisation of P4VP

The phase diagrams were carried out in order to estimate the ability of P4VP to dissolve in water/methanol mixtures. Several flasks of different concentrations of P4VP: P4VP1; P4VP2 and P4VP3 samples in water/methanol were prepared at 25°C. The mixture was left about three hours under shaking, to ensure equilibrium.

2.5 Concentrations of P4VP for titrations

The concentration of the polymer for titrations were 1.6×10^{-4} to 7.98×10^{-3} monomol/l; 20 ml of the solutions were titrated by HCl prepared in water/methanol because P4VP is prepared in water/methanol ($C_{HCl} = 10 \times C_{P4VP}$). The dielectric constant (ε) depends upon the composition of the water/methanol mixture. The dielectric constant ε for mixture of solvent was calculated[17] from the values of ε of each pure solvent pure[18] and empiric equation of Osta[19] for mixture solvent, when water is solvent 1:

$$\varepsilon \approx \varepsilon_1 + [(\varepsilon_2 - 1) (2\varepsilon_2 + 1) / (2\varepsilon_2 - (\varepsilon_1 - 1)] \times x'_2 \, V_2 / V \qquad (2)$$

Where V is the molar volume, calculated for molar volumes of pure solvents V_1 and V_2

$$V = x'_1 V + x'_2 V$$

When x'_1 and x'_2 were molar fractions for solvents 1 and 2.

Polymers are characterized by their average dimensionless charge density parameter ξ[20]

$$\xi = \frac{l_B}{l} \qquad (3)$$

Where l_B is the Bjerrum length and l is the average charge spacing along the contour of the polymer).

$$l_B = \frac{Z_p Z_c e^2}{\varepsilon k_B T} \qquad (4)$$

Where, ε is the dielectric constant, k_B is the Boltzmann constant, T is the absolute temperature, Z_p is the valency of the polyion, Z_c is the valency of the conter-ion and e is the electronic charge)

$$l = \frac{a}{\alpha_i} \qquad (5)$$

Where a is the length of the monomer and α_i is the ionization degree.

The theory of Manning[20] indicates that for $\xi < |z_c|^1$, where z_c is the counter-ion valence, there are no condensed counter-ions. When $\xi > |z_c|^{-1}$, sufficient counter-ions will condense on the polyion to lower the value of the charge density parameter until ξ reaches the critical value $\xi^* = |z_c|^{-1}$

$\xi^* = 1$ for monovalent counter-ions and $\xi^* = 1/2$ for divalent counter-ions

From critical charge density ξ^*, we calculate α_{ic}.

Following Manning[20], for $\alpha > \alpha_{ic}$, the added H$^+$ ions remains in solution and cannot react with the following N base.

The neutralization degree α is calculated by:

$$\alpha = \frac{\left[H^+ \right]}{\left[N \right]} \qquad (6)$$

The water capacity to separate the charges is high compared to that of methanol. Thus, addition of methanol to the mixture decreases the strength of dissociation which becomes very low for 1:1 ratio volume composition. The protonated P4VP is a low charged polyelectrolyte (TABLE 1) because $\alpha_i < 0.4$ in water and in water-methanol mixture.

2.6 Phase diagrams

The phase diagrams were obtained according to the following procedure. The polymer samples were

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TABLE 1: Dielectric constant, Bjerum length and critical ionization degree of P4VP with different contents of water in the solvent mixture at 25°C. $\varepsilon_{methanol} = 33$

% Water	50	60	70	80	90	100
ε	41.16	59.86	71.04	75.89	78.80	78.5
l_B (Å)	13.6	9.35	7.88	7.38	7.17	7.13
α_{ic}	0.188	0.27	0.32	0.34	0.35	0.36
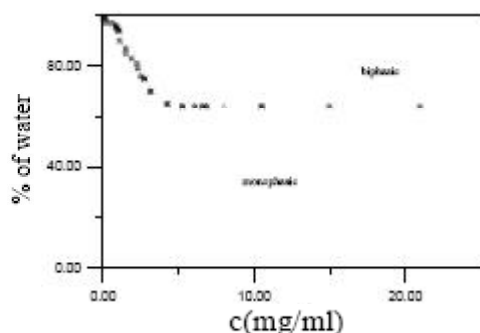
Figure 1: Molecular weight effect on P4VP solubility in water/methanol mixtures at 25°C:- x: P4VP3, o: P4VP2, Δ: P4VP1
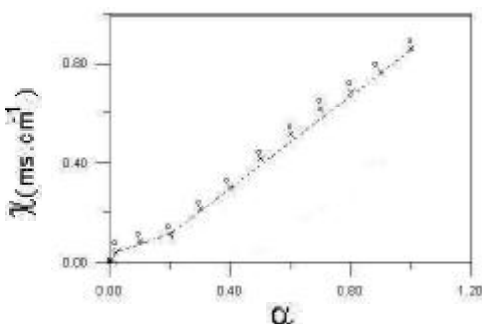
Figure 2: Conductance variation vs α of P4VP solution water/methanol at 25°C:- x: P4VP3, o: P4VP1
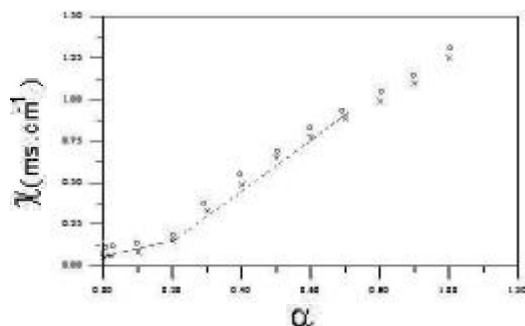

Figure 3: Conductance variation vs α of P4VP solution (2.0×10⁻³ M), in 50 % water/methanol at 25°C. x: P4VP3, o: P4VP1

dissolved in methanol. Equal volumes of polymer solution and solvent were mixed and vigorously stirred until reached equilibrium. The diagram shown in figure 1 has been established by visual observation, three days

after the preparation. Three molecular weight were considered in a large domain concentration between 0.01-20 g/l equivalent to 0.95×10^{-4}–0.19 monomol/l. Phase diagrams are established by plotting water/methanol percentage compositions as a function of the P4VP concentration (Cp).

In figure 1, phase separation is observed when water percentage increases. When the polymer concentration increases, the phase separation becomes more important and the water percentage needed decreases. For low concentrations, polymer gives homogeneous solutions at high water percentage composition. For polymer concentration more than 4 mg/ml (0.038 monomol/l), the polymer becomes non soluble in solvent mixtures rich in water (water percentage>64 %). At high concentration, P4VP forms a large number of intramolecular interactions leading to chain contractions. The diagrams always contain two main regions separated by the demixing curve. The first below, we observe a phase transition and the second above, leading to non transparent solutions. Figure 1 showed also that the P4VP solubility is not dependent on P4VP molecular weight.

Poly(4-vinylpyridine) and proton interactions (P4VP-H⁺)

Conductimetric behaviour

Conductimetry can be used to detect a strong interaction between ions and polyions[21], and therefore, it gives information on the condensation of the counterions on the polyion.

This phenomenon can be followed and studied by using Manning model[20].

Figures 2 and 3 describe the conductivity variation of P4VP solution according to alpha α, at 25°C in 50 % water/methanol solution and for a given P4VP concentrations 1.6×10^{-4} monomol/l and 2.03×10^{-3} monomol/l. The conductance of P4VP solutions increases with α.

At $\alpha_c > 0.2$, we observe that χ increases more rapidly. This indicates that the proton H⁺ bounded on the polymer until critical α, where after the fixation will be more weak. Thus, conductimetric titration provides information on the mobility of the polymer chain as a function of the slope of the conductance curve vs. α[21]. The decrease of the slope from α equal to 0.2 (figures
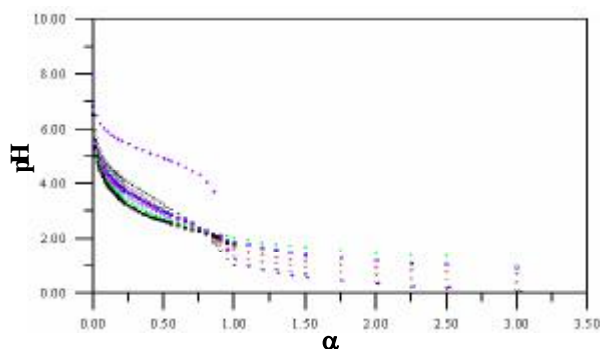
Potentiometric behaviour

Fuoss and Strauss[7] carried out the potentiometric titration of partially protonated poly(4-vinylpyridine) but did not consider the whole range of protonation degree α. The value of pK at α=0.5, was found to be 3.0-3.2. Kirsh[3] used the complete potentiometric titration of P4VP in the ethanol/water mixtures. The results show that both pKa at α=0.5 and pK_0 are considerably less than pKa of ethylpyridine. Satoh[4] showed the same results, in the presence of 0.1 M NaCl or 0.1 M sodium benzenesulfonate in aqueous and in 45 % aqueous ethanol solution.

In figures 4 and 5, are plotted the titration curves of P4VP1 and P4VP3, at different concentrations, and that of ethylpyridine in 50% water/methanol solution. These results indicate that the monomer is more basic than the P4VP of both low and high macromolecular weight. Indeed, it is known that the second proton is less reactive than the first. This effect is observed when a molecule has two or several sites of ionization in a closed space. The ionization energy of a given group is considerably larger if the close sites are already charged.

This effect is well expressed in the case of the polyelectrolytes. The pH decreases with the polymer concentration for both P4VP1 and P4VP3.

The titration curves of P4VP vary with polymer concentrations (figures 4 and 5). For concentrations superior than 2.10^{-3}M, the pH decreases regularly. In contrast, for low concentrations, the curve for 1.6×10^{-4}M concentration is more complex, reflecting the conformational transition between α=0.1 and 0.2. This is typical to the titration of a tight compact conformation in which the cohesive forces keep the pyridinium groups close together, thus increasing the pKa. In this range of α: 0.1–0.2, the electrostatic repulsions begin to exceed the cohesive forces and the compact conformation deals with a decrease of the pKa. The titration curve of the molecule model ethylpyridine is typical of weak base and no special behaviour is observed in this range of α.

Another usual way to plot the pHmetric titration data of polyelectrolytes, is to represent the apparent pKa[22]. The negative logarithm of the apparent dissociation constant, pKa, defined by:

$$pKa = pH + \log\left[\frac{\alpha}{1-\alpha}\right] \qquad (6)$$

Figure 4: Titration curves of P4VP1 in 50 % water/methanol at 25°C :- x:C_{P4VP} = 7.98×10⁻³ M; * : C_{P4VP} =4.06×10⁻³ M; ◊: C_{P4VP} = 3×10⁻³ M; □: C_{P4VP} = 2.42×10⁻³ M; ∇ C_{P4VP} = 2.03×10⁻³ M; o: C_{P4VP} =1.5×10⁻³ M; ⊕ : C_{P4VP}= 7.98×10⁻³ M; ⊞ C_{P4VP} = 7.98× 10⁻⁴ M; ✭ :C_{P4VP}= 1.6×10⁻⁴ M; ♦ :C_{Etpy} = 1.6×10⁻⁴ M
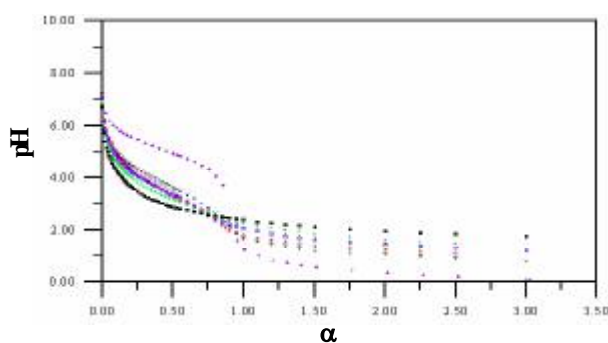
Figure 5: Titration curves of P4VP3 in 50 % water/methanol at 25°C:- x:C_{P4VP} = 7.98×10⁻³ M; *: C_{P4VP} = 4.06×10⁻³ M; ◊:C_{P4VP} = 3×10⁻³ M; □ : C_{P4VP} = 2.42×10⁻³ M; ∇: C_{P4VP} =2.03×10⁻³M; o:C_{P4VP} = 1.5×10⁻³M ; ⊕ :C_{P4VP} =7.98×10⁻⁴ M; ⊞ : C_{P4VP} = 4.06×10⁻⁴ M; ✭ :C_{P4VP} = 1.6×10⁻⁴ M; ♦ C_{Etpy} = 1.6×10⁻⁴ M
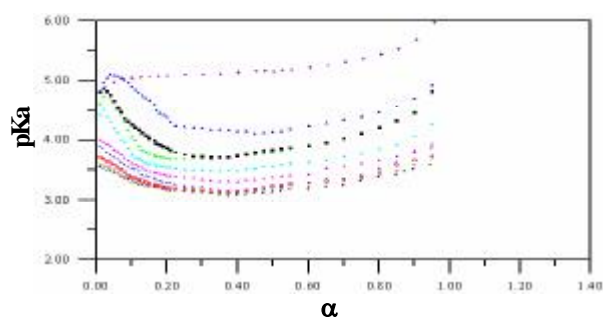

Figure 6 : Variation of the apparent dissociation constant pKapp vs. α for P4VP1in 50 % water/methanol at 25°C:- CP4VP = 0.798×10⁻³ M; ◊CP4VP = 4.06×10⁻³ M; □:C_{P4VP} = 3×10⁻³ M; o: C_{P4VP} = 2.42×10⁻³ M; ∇:C_{P4VP} = 2.03×10⁻³ M; ★: C_{P4VP} = 1.5×10⁻³ M; *C_{P4VP} = 7.98×10⁻⁴M; ■ : CP4VP =4.06×10⁻⁴ M; ΔC$_{P4VP}$ = 1.6×10⁻⁴M; ♦ C_{EtPy} = 1.49 × 10⁻⁴ M.

2 and 3) indicates an increase of the average dimension of the polymer.

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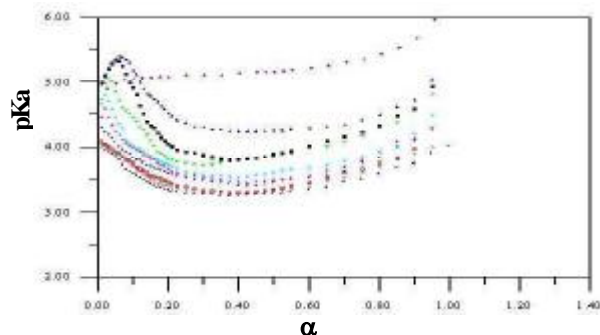**Figure 7: Variation of the apparent dissociation constant pKapp vs. a for P4VP3 in 50 % water/methanol at 25 °C:-**
+: $C_{P4VP} = 7.98\times10^{-3}$M; ◊: $C_{P4VP} = 4.06\times10^{-3}$M; □:$C_{P4VP} = 3.10$-3M; o:$C_{P4VP} = 2.42\times10^{-3}$M; ∇: $C_{P4VP} = 2.03\times10^{-3}$M; ★: $C_{P4VP} = 1.5\times10^{-3}$M; *: $C_{P4VP} = 7.98\times10^{-4}$M; $C_{P4VP} = 4.06\times10^{-4}$M; Δ:$C_{P4VP} = 1.6\times10^{-4}$M ; ♦$C_{Etpy} = 1.49\times10^{-4}$M

is not constant. But, it increases or decreases with α for polyelectrolytes. The pKa can be expressed by a sum of two terms as[23]

$$pKa = pK_0 + \frac{0.434}{RT}\left(\frac{\delta Gel}{\delta\alpha}\right) \tag{7}$$

where K_0 is the intrinsic dissociation constant, pH is the acidity or alkalinity of a solution, α is the degree of protonation, T absolute temperature, R the gas constant and Gel is the electrostatic Gibbs free energy of dissociation of one mole of protons. The plots of pKa versus α at different concentrations of the P4VP1 and P4VP3 polymers, are shown in figures 6 and 7.The pKa decreases with the ionization degree up to a minimal value 0.2 for concentrations ranging from 3×10^{-3} to 0.01M. The pKa is stabilized in the range: α=0.2-0.6. Above α>0.6, the pKa grows slightly. For concentrations ranging between 2.03×10^{-3} and 1.6×10^{-4}M, the pKa increases at the beginning of the neutralization for very low values until reaching a maximum, after which the pKa decreases quickly with α. Then, pKa is stabilized in α range 0.2-0.6. After α=0.6, the pKa restarts growing. The pKa values of the P4VP1 and P4VP3 are weaker than that of the 4-ethylpyridine which presents more great basic strength. pKa maximum values of P4VP1 and P4VP3 for 1.6×10^{-4}M concentration are higher than the corresponding ethylpyridine pKa. The pKa values of the sample of strong mass P4VP1 are lower than those of sample P4VP3 of low mass. Furthermore, more the molecular weight is high, more pKa of P4VP polymer is weak. Thus, an increasing in

the molecular weight decreases the reactivity of pyridinic bases. It is also observed that pKa decreases with the P4VP concentration in the range 0-1M. For weak polymer concentrations, electrostatic interactions induce an easy expansion chains. For the concentration range 1.06×10^{-4}-2.03×10^{-3} monomol/l, the P4VP has an helicoïdal conformation and the curve maximum corresponds to a maximum active nitrogen atoms. The charged N^+ far from the carbon backbone makes possible this conformation, with a minimal energy.

In Contrast, with Mandel conclusions[24] which considers that the concentration influence could be neglected, we show here that the pKa variation according to α depends on both concentration and P4VP molecular weight. Kirsh[6] showed that pKa remains constant in a large range of molecular weight between 3×10^4 and 10^6 g.mol^{-1} and for concentration range 2×10^{-2}-2×10^{-3} monomol/l. In our work, we used a large domain concentration and two different molecular weights compared to the Kirsh data[6]. For the same concentrations, we found the same experimental results. The small quantitative difference is due to different natures of the used mediums. The change of the curves shape for the much diluted concentrations, in the vicinity of α=0.01, enables us to conclude that the P4VP exists initially under different conformation. An interesting behaviour is observed for pKa variation according to α, for much diluted concentrations. The pKa show a maximum ranging between 0.01 and 0.08. For low concentrations, changing curves is explained by hydrophobic and hydrogen bonds properties of the pyridinium groups. This behaviour is connected to the conformational transition. Thus, for the diluted system, the low basicity observed with the increasing concentration can be attributed to the missing hydrogen bonds.

Several Authors consider that the pK_0 is an intrinsic value with the monomeric unit and takes the value of the pKa acid or basic monomer[25]. Other authors deduce the pK_0 starting from the variations from pK according to α, while extrapolating. Arnold and coll.[26] and Katchalsky[27] obtain pK_0 by respectively using solutions slightly concentrated in the presence of salt for low molecular weights. For the P4VP, we used the pK_0 ethylpyridine and those found starting from the adjustment of Mandel[28]. Mandel[28] has suggested to
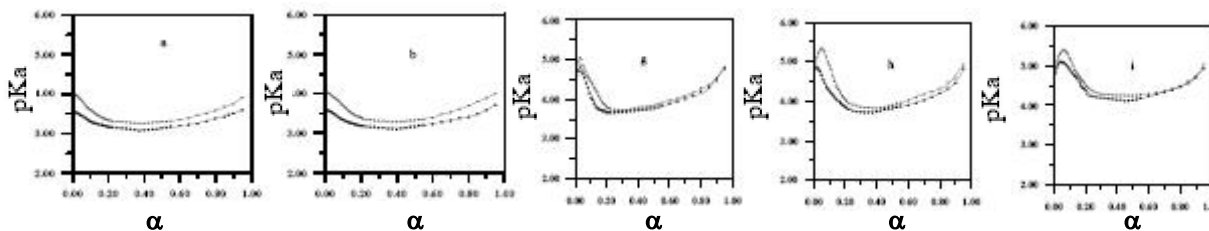
Figure 8: Ajustment of pKa by polynomial Mandel equation for P4VP1 and P4VP3:- a: C_{P4VP} = 7.98×10-3 M; b: C_{P4VP} = 4.06×10-3 M; g: $C_{P4VP}C_{P4VP}$ = 7.98×10-4 M; h: C_{P4VP} = 4.06×10-4 M; i: C_{P4VP} = 1.6×10-4 M; o: P4VP3 · P4VP1
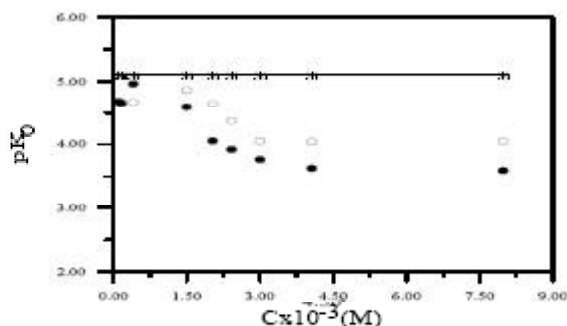

Figure 9: Variation of the pK0 vs. the polymer concentration:- ·: P4VP1, o : P4VP3 et *: Etpy

TABLE 2: pK_0 Values of the polymers and monomer at 25°C in 50 % water/methanol solution

Monomer, polymer	pK_0
4Etp	5.09
P4VP3	4.04-4.64
P4VP1	3.59-4.67

adjust the experimental variations of pKa by a polynomial function with

$$pKa = pK_0 + \phi_1\alpha + \phi_2\alpha^2 + \dots \qquad (8)$$

In order to represent the variation of the pKa according to the α neutralization degree, within the limits of experimental errors, we chose the eight degree polynomial, which gives the best correlations (figure 8) between the pKa experimental and calculated results.

Figure 9 shows the variation of pK_0 vs.α. The pK_0 values of the monomer 4-ethylpyridine, the P4VP1 and P4VP3 are different.

It is seen from the TABLE 2 that pK_0 of the monomer analogue is higher than those of the P4VP3 than the P4VP1 for the concentrations ranging between (7.98×10⁻³ monomol/l and 7.98×10⁻⁴ monomol/l).

The pK_0 of polymers increases when the concentration decreases to become close to the pK_0 of the ethylpyridine for concentrations (4.06×10⁻⁴-1.06 ×10⁻⁴ monomol/l). The dissociation constant of pyridine function of polymers in the absence of electrostatic interaction (pK_0) are lower than for the monomer

analogue 4-ethylpyrine and depend on molecular weight and concentration of P4VP.

Effect of concentration

P4VP is not soluble in neutral medium. But, it is soluble in acidic aqueous solution and in water/methanol mixture. Even, in very diluted HCl solution, some of the nitrogen rings are protonated. As the concentration of HCl increases, the number of neighbouring charged rings increases. As a consequence of repulsive interactions between neighbouring charged rings, the P4VP polymer coil expands and assumes a rod-like conformation. This conformational reorganization causes a decrease in the polymer basicity. When the titration is carried out, at polymer concentration superior than 1.6×10⁻⁴ monomol/ l, the titration curve of P4VP drastically changes. Thus, we can assume that the compact conformation is stabilized by hydrogen bonds, which are destroyed at high polymer concentration.

CONCLUSION

A set of poly(4-vinylpyridine) were synthesized by free radical polymerization and characterized by ¹HNMR. The weight-average molar mass were determined by light scattering and viscosimetry. The P4VP-H⁺ interactions was studied at 25°C by conductimetry and potentiometry in 50 % water/ methanol solution to obtain the total range of neutralization (0-1). The effect of the molecular weight and P4VP concentration, on the potentiometric behaviour, was investigated. The P4VP critical concentration Cp* (4 mg/ml) at phase separation, is expected to be independent on the P4VP molecular weight. pKa and pK_0 depend on both P4VP concentration and molecular weight. The increasing of the protons H⁺ caused an increasing of the pyridinium

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groups witch destroyed the compact conformation for the P4VP in aqueous/methanol solutions. Conformation changing are observed at $\alpha=0.2$ (degree of neutralization) showing that an equilibrium exists between N and N^+ in the present system. Good agreement was obtained between the experimental potentiometry and conductimetry results.

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