

# Viscometric Study of some Polyzwitterions based on poly(4-vinylpyridine)

STEFANIA RACOVITA<sup>1</sup>, SILVIA VASILIU<sup>1</sup>, CEZAR DORU RADU<sup>2</sup>, LENUTA PROFIRE<sup>3</sup>, LAURA CHECHERITA<sup>\*\*</sup>, LILIANA FOIA<sup>3</sup>

<sup>1</sup>"Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Vodă Alley, 700487, Iași, Romania

<sup>2</sup>"Gh. Asachi" Technical University, Faculty of Textiles-Leather and Industrial Management, 29 Mangeron Bd., 700500 Iasi, Romania

<sup>3</sup>"Gr.T.Popa" University of Medicine and Pharmacy, Faculty of Dental Medicine, 16 Universitatii Str., 700115, Iasi, Romania

*The viscometric behavior of the poly(carboxybetaines) possessing structural units of [4-vinyl-1-(2-carboxymethyl) pyridinium betaine] and [4-vinyl-1-(2-carboxyethyl) pyridinium betaine] was investigated. Deionized water as well as CaCl<sub>2</sub> and NaCl aqueous solutions of different concentrations were used as solvents. The solubility and viscometric behaviors of the two poly(carboxybetaines) were strongly dependent on the chemical nature of the spacer between N<sup>+</sup> and COO groups and the nature of the solvent. Einstein-Simha and Rao equations were used to assess the intrinsic viscosity values.*

*Keywords: poly(carboxybetaines), Rao and Einstein-Simha equations, water-soluble polymers, intrinsic viscosity*

Ionic polymers may be divided into two groups: polyelectrolytes (PE) and polyzwitterions (PZ) [1]. The polyelectrolytes have ionisable functional groups that are either anionic or cationic. The charge may be along or pendent to the polymeric chain and they are balanced by small counterions. Zwitterionic polymers have both cationic and anionic charges, along or pendant, to the same polymeric chain [2, 3].

One of the major classes of PZ is represented by the polybetaines. At these polymers the two opposite charges are located in the same repeat unit, with an alkyl group between them. The positive charge is due to a quaternary ammonium group whereas the anionic charge may be due to carboxylate (polycarboxybetaines/polycarboxybetaine), sulfonate (polysulfobetaines) or phosphate/phosphonate/phosphinate group (polyphosphobetaines).

The literature data show that the polybetaines are performed by three ways: (i) betainization of an acrylic or vinylic monomer which contains a tertiary amine group followed by (co) polymerization of the betaine monomer; (ii) betainization of a previously performed polymer containing tertiary amine group, so-called precursor, by the suitable polymer-analogous reaction; (iii) the Michael addition reaction [4]. The second synthesis pathway was especially used for the achievement of poly(carboxybetaines) based on poly(4-vinylpyridine) (P4VP). The betainization of P4VP was routinely by the following protocol: quaternization of the polymer with esters of the haloalkylencarboxylic acids, a nucleophilic substitution reaction type, followed by the hydrolysis of the ester groups and the removal of the respective haloacids [5].

Consequently PZ, and polybetaines represent high dipolar materials with a wide spectrum of unique and specific properties both in solution and in solid state [2-4, 6]. Thus, in the solution they have an "anti-polyelectrolyte" behaviour involving low solubility in water but greatly enhanced solubility and extensive chain expansion with increasing of the salt concentration. In contrast to PE, PZ in the solid state are capable of simultaneous interaction with both ions of the added electrolytes leading to

homogenous blends when PZ are mixed with some inorganic salts in equimolar amounts. In addition, poly(carboxybetaines), are pH-sensitive polymers in contrast to poly(phosphobetaines) and poly(sulfobetaines). This behaviour is due to the protonation of carboxylate groups in acid medium which determines the transformation of poly(carboxybetaines) to corresponding cationic polyelectrolytes [7].

The polybetaines have applications in water treatment, petroleum recovery, viscosifications, formulation of coatings and cosmetics. Also, polybetaines, as such or by copolymerization of acrylic monomers chemically modified, have a wide variety of applications in biocompatible medical devices and additives for antifouling coatings because of their antimicrobial properties [8-13].

In this paper were applied two empirical equations to determine the intrinsic viscosity values for two polycarboxybetaines based on poly(4-vinylpyridine) namely these with [4-vinyl-1-(2-carboxymethyl) pyridinium betaine] (P4VPB-1) and [4-vinyl-1-(2-carboxyethyl) pyridinium betaine] (P4VPB-2) structural units in amount higher than 90%. The results could be useful in finding new applications for these polybetaines in medicines.

## Experimental part

### Materials

Poly(4-vinylpyridine) ( $\bar{M}_v = 60.000$  g/mol), acrylic acid and sodium chloroacetate were purchased from Aldrich Chemical Co.. The acrylic acid was distilled in vacuum prior to use.

### Synthesis of poly(carboxybetaines)

The reactions between P4VP with sodium chloroacetate and acrylic acid were performed as previously shown [5]. The synthesis of poly(carboxybetaines) is depicted in figure 1.

The structures of the polymers obtained by the reaction of poly(4-vinylpyridine) as well as their molar transformation degrees values were determined by using <sup>1</sup>H NMR spectra.

\* email: checherita.laura@gmail.ro

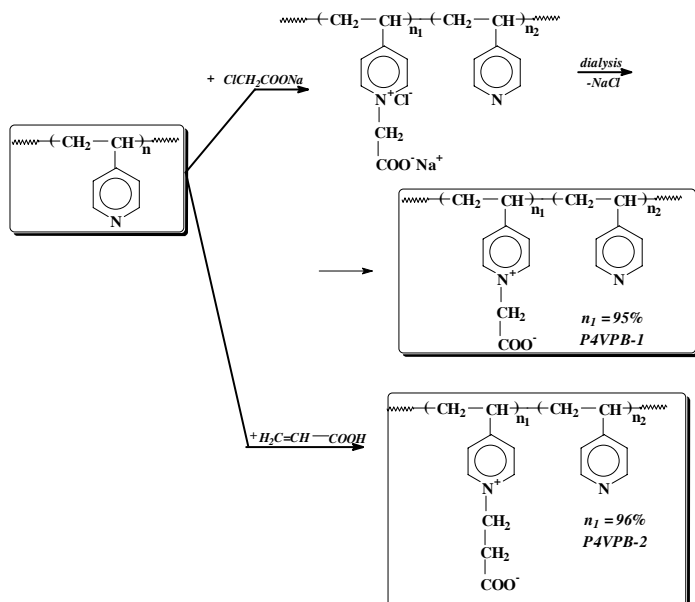


Fig. 1. Synthesis of poly(carboxybetaines)

$^1\text{H}$  NMR spectra were recorded in  $\text{CD}_3\text{OD}$  at 90MHz on a Varian EM 390 spectrometer. The signal from trace of  $\text{CHD}_2\text{OD}$  (3.42ppm) was used as a reference signal.

The spectra of P4VP, P4VPB-1 and P4VPB-2 show the significant differences between the aromatic proton chemical shifts in neutral and ionic structures. The two aromatic proton signals of 4-substituted pyridine ring are shifted from about 6.8 and 7.3 ppm, for neutral units, to about 7.5 and 8.8ppm, respectively, for betaine units. The spectral difference between the two kinds of zwitterionic polymer units is that the units 4VPB-1 generates a singlet signal at 5.2ppm for  $\text{N}^+\text{CH}_2\text{COO}^-$  protons, while the groups  $\text{N}^+\text{CH}_2\text{CH}_2\text{COO}^-$  show signals at 4.8 and 2.9ppm.

#### Viscometric behaviours and data processing

Solution viscosities were determined with an Ubbelohde viscometer at  $25.0 \pm 0.05^\circ\text{C}$  (flow time 168s for distilled water). All the viscometric measurements were achieved in triplicate and the average values were plotted. The polymer samples were dissolved in solvent (water or salt solutions) to yield stock solutions. These solutions were subsequently diluted with the appropriate above-mentioned solvents and allowed to age for 24 h before the viscometric determinations.

The type of behaviour was established from reduced viscosity ( $\eta_{\text{red}}$ ) versus polymer mass concentration ( $c$ ) plots. The values of the intrinsic viscosity,  $[\eta]$  were estimated by means of the empirical or semi-empirical equations of Einstein-Simha (1) and Rao (2) [14, 15]:

$$\eta_r = 1 + [\eta]c \quad (1)$$

where  $\eta_r$  is the relative viscosity.

$$\frac{1}{2(\eta_r^{1/2} - 1)} = \frac{1}{[\eta]c} - \frac{a-1}{2.5} \quad (2)$$

where  $a$  is the specific coefficients ( $a = 1/\Phi_m$ ,  $\Phi_m$  is the maximum volume fraction to which the suspended

particles can pack). When  $2(\eta_r^{1/2} - 1)^{-1}$  is plotted as a function of reciprocal of concentration (g/dl), the slope yields the intrinsic viscosity and the intercept gives the value of  $a$  and consequently  $\Phi_m$ . The  $\Phi_m$  value is a measure of the quality of solvent. The lower  $\Phi_m$  values indicating the lower quality of solvent and polymer aggregation. When a  $\Phi_m$  value is near to or equal to unity indicate a good solvent.

## Results and discussions

### Solubility of polycarboxybetaines

Observations about the dissolution of the poly(carboxybetaines) in discussion are presented in table 1.  $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{CdCl}_2$  were chosen as representative salts for generation of monovalent, divalent and transitional metal ions respectively. About the dissolution in water with  $\text{CdCl}_2$ , it was observed that the poly(carboxybetaines) dissolve initially but precipitate during or immediately after dissolution. Such a behaviour might be related with the property of  $\text{Cd}^{2+}$  ions to form coordination bonds with the groups  $\text{COO}^-$ , besides the ionic bonds.

### Viscometric behaviours

P4VPB-1 is not soluble in pure water, but is soluble in aqueous salt solutions (i.e.,  $\text{NaCl}$  and  $\text{CaCl}_2$ ). The insolubility in water may be explained by the chemical structure of P4VPB-1. Thus, because the chemical bond distance between the counterions in the same zwitterionic group,  $\text{N}^+\text{CH}_2\text{COO}^-$ , is too short for cyclization, the charge neutralization leads to a network with ionic crosslinks, which are not too dense or strong, probably. Such a network dissolves in salty water when the salt ion-polymer interactions are strong enough and fragmented to cancel the crosslinks.

The viscometric behaviours of P4VPB-1 in 0.05 and 0.5 M aqueous solutions of  $\text{NaCl}$  and  $\text{CaCl}_2$  are plotted in figure 2.

From the plots of the figure 2 can be observed the following aspects:(i) the reduced viscosities increasing with salt concentration; (ii) the reduced viscosities values

**Table 1**  
SOLUBILITY OBSERVATION ON THE POLY(CARBOXYBETAINES) STUDIED

	Pure water	Aqueous solutions of salts		
		$\text{NaCl}$	$\text{CaCl}_2$	$\text{CdCl}_2$
P4VPB-1	-	+	+	-
P4VPB-2	+	+	+	-

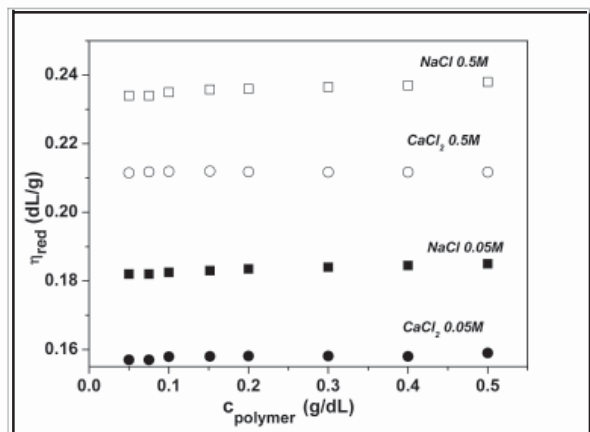


Fig. 2. The reduced viscosity as a function of P4VPB-1 concentration dissolved in NaCl and CaCl<sub>2</sub> aqueous solutions, at 25 °C

decreasing with the salt cation valence and (iii) the reduced viscosities are insensitive to the polymer concentration, i.e., P4VPB-1 exhibits a behaviour of hard-sphere suspensions in all the solvents. The last characteristic has been also reported for some poly(sulfobetaines) [14]. For such systems, it is indicated to evaluate the viscosity data using a modified Einstein-Simha equation (1). Also, the Rao equation (2) was used for calculation of the intrinsic viscosity of the P4VPB-1. This equation has been applied first in the case of neutral polymers [9] and then for the polyelectrolytes [16-20].

Figures 3 and 4 illustrate the plots from the Einstein-Simha and Rao equations from P4VPB-1.

The linearity of the data and an intercept value of 1 (fig. 3) confirm that P4VPB-1 behaves as a suspension in aqueous solution of salts.

Viscosimetric data for P4VPB-1 analyzed by Einstein-Simha and Rao equations led to the  $[\eta]$  and  $\Phi_m$  values given in table 2.

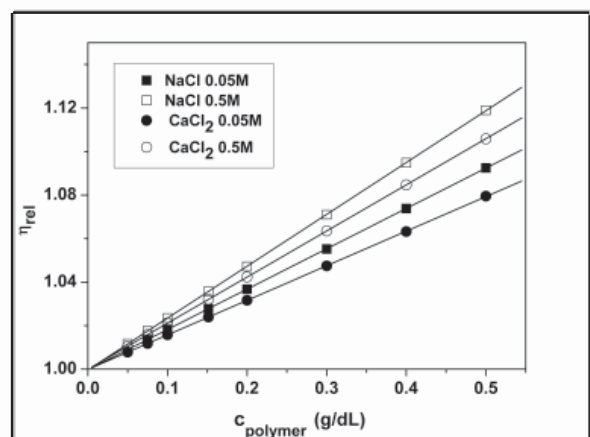


Fig. 3. Representation of the Einstein-Simha equation for P4VPB-1 in aqueous solutions of NaCl and CaCl<sub>2</sub> at 25 °C

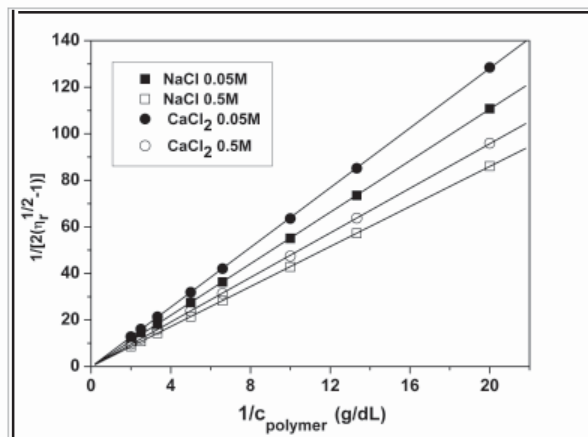


Fig. 4. Representation of the Rao equation for P4VPB-1 in aqueous solutions of NaCl and CaCl<sub>2</sub> at 25 °C

From the data listed in table 2 one can say that the  $[\eta]$  values determined by the two equations are in good agreement. The intrinsic viscosity, which is a measure of the macromolecular chain extension, is lower for CaCl<sub>2</sub> solution than for NaCl solutions of the same molar concentration (table 2). This fact may be explained by two opposite effects of the divalent cations, (i) detachment of polymer-polymer ionic bonds, and (ii) coupling as two COO<sup>-</sup> groups, unlike the monovalent cations, which produce only concentration of polymer-polymer interactions. Also, the  $\Phi_m$  value is low for CaCl<sub>2</sub> solution than for NaCl solutions and increase with the salt concentration.

Table 2 shows also that the intrinsic viscosity, calculated by these two equations, increases with the salt concentration. This characteristic and the insolubility in pure water suggests that P4VPB-1 behaves as an "anti-polyelectrolyte" when is dissolved in salt aqueous solutions.

The solubility of P4VPB-2, which is better than that of P4VPB-1, allowed viscosity determinations within water and salt solutions. Figure 5 displays the dependence of the reduced viscosity on the polymer concentration.

The shape of the plots from figure 5 shows that P4VPB-2 has a typical viscosimetric behaviour of zwitterionic polymer in pure and salty water, i.e. the reduced viscosity does not depend on the polymer concentration [10-13, 17-22]. Also, the viscosity data may be analyzed through of Einstein-Simha and Rao equations (table 3).

The data presented in table 3 are in good agreement with  $[\eta]$  values calculated by these two equations. From the table 3 can be mentioned the following aspects: (i) the  $[\eta]$  and  $\Phi_m$  values increasing with increasing salt concentration; (ii) the salts which contain divalent ions determine the lower  $[\eta]$  and  $\Phi_m$  values; (iii) in the water is observed the highest  $[\eta]$  value associated with the low  $\Phi_m$  value. Last observation could be explained as due to the fact that in pure water this polymer can exist as aggregations of polymer chain with spherical conformations. The addition of small salt amounts leads

Sample	Solvent	$[\eta]_{\text{Einstein-Simha}}$ (dL/g)	$R^2_{\text{Einstein-Simha}}$ *	$[\eta]_{\text{Rao}}$ (dL/g)	$R^2_{\text{Rao}}$ *	$\Phi_m$
	NaCl 0.05M	0.185	0.999	0.181	0.999	0.754
P4VPB-1	NaCl 0.5M	0.238	0.999	0.233	0.999	0.913
	CaCl <sub>2</sub> 0.05M	0.159	0.999	0.156	0.999	0.716
	CaCl <sub>2</sub> 0.5M	0.212	0.999	0.209	0.999	0.882

$R^2$  correlation coefficient

**Table 2**  
VARIATION OF THE INTRINSIC VISCOSITY AND  $\Phi_m$  OF P4VPB-1 AS A FUNCTION OF THE SALT CONCENTRATION

Sample	Solvent	$[\eta]_{\text{Einstein-Simha}}$ (dL/g)	$R^2_{\text{Einstein-Simha}}$ *	$[\eta]_{\text{Rao}}$ (dL/g)	$R^2_{\text{Rao}}$ *	$\Phi_m$
P4VPB-2	H <sub>2</sub> O	0.325	0.999	0.306	0.999	0.401
	NaCl 0.05M	0.187	0.999	0.182	0.999	0.678
	NaCl 0.5M	0.323	0.999	0.318	0.999	0.904
	CaCl <sub>2</sub> 0.05M	0.184	0.999	0.177	0.998	0.544
	CaCl <sub>2</sub> 0.5M	0.285	0.999	0.279	0.999	0.807

R<sup>2</sup> correlation coefficient

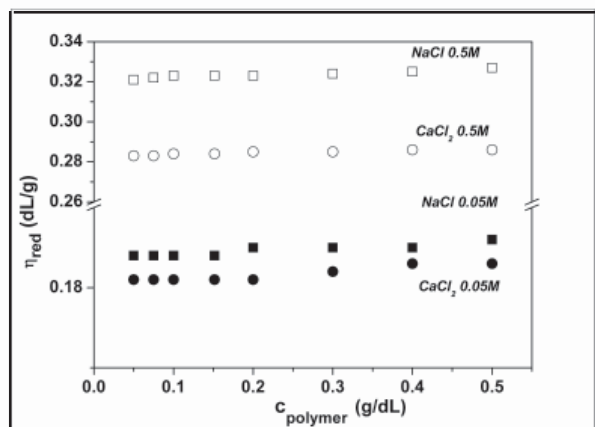


Fig. 5 The dependence of reduced viscosities on polymer concentration for P4VPB-2

to the breakup of the inter- and intrachain associations, therefore to the decrease of  $[\eta]$  while the higher salt amounts determine the individual polymeric chain extension and the  $[\eta]$  increase as well.

### Conclusions

The study provides information about the viscosimetric behaviour of the two pol(carboxybetaines) based on poly(4-vinylpyridine). From the studies achieved it was observed the anti-polyelectrolyte behaviour for P4VPB-1. P4VPB-2 is soluble both in water and aqueous solution of salts. The solubility in water is due to the possibility of an inner-salt structure, which yielded to the neutralization between N<sup>+</sup> and COO<sup>-</sup> in the same betaine unit. In water this structure is stronger than in aqueous solution of salts because water is a poorly solvent for P4VPB-2. The experimental data for these polymers were plotted based on Einstein-Simha and Rao equation terms, when very close values for  $[\eta]$  were obtained.

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**Table 3**  
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