Solution Properties of Three Polyzwitterions Based on Poly(N-vinylimidazole)

Stefania Racovita*, Silvia Vasiliu, and Violeta Neagu

"Petru Poni" Institute of Macromolecular Chemistry, 700487, Iasi, Romania

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ABSTRACT

The solution properties of the poly(carboxybetaine)s possessing structural units of [1-vinyl-3-(1-carboxymethyl) imidazolium betaine] (PNVIB-1); [1-vinyl-3-(2-carboxyethyl) imidazolium betaine] (PNVIB-2) and [1-vinyl-3-(2-carboxyisopropyl) imidazolium betaine] (PNVIB-3) were investigated by viscometric measurements and potentiometric titration. Deionized water as well as CaCl₂ and NaCl aqueous solutions with different concentrations and two alcohols, i.e., methanol and ethanol were used as solvents. The solubility and viscometric behaviours of three poly(carboxybetaine)s were strongly dependent on the chemical nature of the spacer between N⁺ and COO⁻ groups and the nature of the solvent. From the studies achieved the polyelectrolyte behaviour of PNVIB-2 in methanol and PNVIB-3 in all the solvents as well as an anti-polyelectrolyte behaviour of PNVIB-2 in water were all observed. Fuoss and Rao equations were used to assess intrinsic viscosity, [η], values in the case of polymers with polyelectrolyte behaviours as well as Einstein-Simha and Rao equations in the case of the polymer with anti-polyelectrolyte behaviour. Using Henderson-Hasselbach equation and potentiometric titrations of aqueous solutions of poly(carboxybetaine)s with 0.5 M HCl the apparent pKₐ values were determined. These values are strongly dependent on the solvent nature. Also, when the water is used as solvent for polymers, it is observed that the PNVIB-2 and PNVIB-3 present the lowest pKₐ values, because of the lowest binding ability of the H⁺ by COO⁻ groups.

INTRODUCTION

It is well known that, as a function of electrical charge, the polymers are divided in neutral and ionic polymers, the latter being classified in polyelectrolytes and polyzwitterions.

A major class of polyzwitterions includes poly(betaine)s which can be divided according to their anionic groups in: poly(sulphobetaine)s, poly(carboxybetaine)s and poly(phosphobetaine)s.

The poly(betaine)s are dipolar species, in which the cationic and anionic groups are separately bound to the same monomer unit and can be completely dissociated in a medium of sufficient dielectric permittivity.

A careful analysis of the literature data shows that the poly(carboxybetaine)s perform in three main ways: (i) betainization of a previously performed polymer...
containing tertiary amine groups, so-called precursor, by the suitable polymer-analogous reactions; (ii) betainization of an acrylic or vinylic monomer which contains a tertiary amine group followed by (co) polymerization of the betaine monomer or (iii) the Michael addition reaction [1-3]. The first method was especially used for the poly(carboxybetaine)s based on poly(4-vinylpyridine) and poly(N-vinyl-imidazole).

Many studies about the solution properties of poly(carboxybetaine)s are already reported. These refer to (i) solubility measurements namely, determinations of CSC [the critical salt concentration, which represents the concentration of salt required to promote the solubility of the poly(carboxybetaine) in aqueous salt solution], for poly(carboxybetaine)s insoluble in water, (ii) description of viscometric behaviour in aqueous solutions of various ionic strengths [4-6], and (iii) determination of "apparent" ionic constants (pKa) by means of potentiometric titrations [6-9]. Also, the aggregation of chains has been investigated by laser light scattering and ζ-potential measurements [10,11].

The poly(betaine)s are polymers with growing scientific and commercial interest [12]. Thus, these polymers have a structural similarity with peptides and living matters serving as their models and the commercial interest is determined by the possibility to achieve some interesting materials such as, inorganic-organic hybrids, polymeric sorbents for saline solutions, materials with ionic conductivity, agents for enhanced oil recovery, surface covering layers of the biomaterials to improve their hemocompatibility.

The aim of the current research was to study some important solution properties of the three poly(carboxybetaine)s based on poly(N-vinylimidazole) namely, those which contain structural units of \[1\text{-vinyl-3-(1-carboxymethyl) imidazolium betaine}\] (PVIB-1); \[1\text{-vinyl-3-(2-carboxyethyl) imidazolium betaine}\] (PVIB-2) and \[1\text{-vinyl-3-(2-carboxy-isopropyl) imidazolium betaine}\] (PVIB-3). The novelty of this work is the use for the first time of the Rao equation in the interpretation of poly(carboxybetaine)s viscometric behaviours. The results could be useful in finding new applications for these poly(carboxybetaine)s.

EXPERIMENTAL

Materials

Acrylic acid, methacrylic acid and N-vinylimidazole were obtained from Aldrich Chemical Co. and distilled in vacuum prior to use. Sodium chloracetate was purchased from Aldrich Chemical Co.

Precursor Synthesis

Poly(N-vinylimidazole) (PVNI) was obtained by free radical polymerization of N-vinylimidazole in benzene under nitrogen atmosphere with AIBN as initiator. The polymer was precipitated as a white powder. The solid was separated by filtration and dried at 40°C. PVNI was purified by dissolving in methanol and precipitating using acetone twice. Finally, the polymer was dialyzed against distilled water using dialysis tubing. PVNI was isolated by lyophilization and dried over P2O5 in vacuum at room temperature and then it was characterized by viscosity average molar mass determination. Viscosity average molar mass was calculated using the Mark-Houwink-Sakurada equation:

\[
\eta = K(M_v)^{\alpha}
\]

where \(K = 122 \times 10^{-3}\ \text{mL/g}\) and \(\alpha = 0.51\) in 0.1 M NaCl at 25°C [13].

The \(\bar{M}_v\) value of PVNI was found to be 305,000 g/mol.

Poly(carboxybetaine)s Synthesis

The reactions between PVNI with sodium chloracetate, acrylic acid and methacrylic acid were performed as previously shown [3]. Thus, in a 0.25-L flask equipped with a stirrer, refrigerator and thermometer was charged with 5 g of PVNI and 100 mL double distilled water. After the dissolution of the polymer under stirring the reagent (7.44 g sodium chloroacetate; 4.5 mL acrylic acid or 4.42 mL methacrylic acid) was added. The reaction mixtures were reacted at 60°C, for 120 h for PVNI-1, 48 h for PVNI-2 and 240 h for PVNI-3, respectively. At the end each content of the flask was discharged into a dialysis tubing (\(M_w = 10,000-12,000\ \text{g/mol}\) and dialyzed against distilled water. After purification the polymers were isolated by lyophilization and dried.
over P2O5 in vacuum at room temperature.

The molecular weights of the studied poly(carboxybetaine)s have been determined in the previous work by light scattering. Thus, PNVIB-1, PNVIB-2 and PNVIB-3 in 0.5 M NaCl possess a $M_w = 389.000 \text{ g/mol}$, $M_w = 490.000 \text{ g/mol}$ and $M_w = 805.000 \text{ g/mol}$, respectively [11].

The synthesis of poly(carboxybetaine)s is depicted in Figure 1.

$^1$H NMR spectra of aqueous solutions recorded at 400 MHz with a Bruker DRX spectrometer were used to confirm the chemical structure and to determine the fraction of betaine units. The spectra of PNVIB-1, PNVIB-2 and PNVIB-3 show the following signals specific to the betaine units: signals at 4.80 ppm for the methylene protons in N$^+\text{CH}_2\text{COO}^-$ groups of PNVIB-1, signals at 4.4 and 2.75 ppm for the methylene protons belonging to N$^+\text{CH}_2\text{CH}_2\text{COO}^-$ groups, and quasi-singlets at 4.22, 2.93 and 1.17 ppm for the three proton types in N$^+\text{CH}_2\text{(CH)CH}_3\text{COO}^-$ groups of PNVIB-3.

The chemical structure was determined from the relative intensities of the signals derived from the added and parent groups. Therefore, the imidazole aromatic protons H2 and H3 gave a complex signal ($S_t$) placed at 7.3-7.7 ppm, the intensity of which is proportional with the total number of mers, while the signals used as measure for the number of betaine units were: the singlet at 4.80 ppm ($S_1$) for PNVIB-1, the quasi-singlet at 4.65 ppm ($S_2$) for PNVIB-2, and the quasi-singlet at 1.17 ppm ($S_3$) for PNVIB-3. The content of betaine units was calculated with the equations: $S_1/S_t$ for PNVIB-1, $S_2/S_t$ for PNVIB-2, and $(S_3/3)/(S_t/2)$ for PNVIB-3.

Methods

Viscometric Behaviours and Data Processing

Viscometric measurements of the poly(carboxybetaine)s were carried out using Ubbelohde viscometer (flow time 168 s for distilled water) at 25.0 ± 0.05°C. All the viscometric measurements were achieved in triplicate and the average values were plotted. The polymer samples were dissolved in solvent (water, alcohol 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 ($\eta_{\text{red}}$ or $\eta_{sp/c}$) versus polymer mass concentration (c) plots. Depending on the type of behaviour, the values of the intrinsic viscosity were estimated by means of the empirical or semi-empirical equations of Einstein-Simha (1), Rao (2) and Fuoss (3) [14-16]:

![Figure 1. Synthesis of poly(carboxybetaine)s.](image-url)
\[ \eta_r = 1 + [\eta]c \]  
\[ \frac{1}{2(\eta_r^{1/2} - 1)} = \frac{1}{[\eta]c} - \frac{a - 1}{2.5} \]  
\[ \eta_{sp} = \frac{[\eta]}{[1 + Be^{1/2}]} \]

where \( \eta_r \) is the relative viscosity, \( \eta_{sp} \) is the specific viscosity (\( \eta_{sp} = \eta_r - 1 \)), \( a \) and \( B \) are the specific coefficients.

**Potentiometric Titrations and Data Processing**

Potentiometric titrations were conducted to measure pH at 25.0 ± 0.5°C using a Hach Sension 3 with gel filled pH electrode and temperature probe in triplicate and the average values were plotted. The titrations were carried out with 0.5 M HCl for poly(carboxybetaine)s dissolved in deionized water and 0.5 M NaCl of 0.2 g polymer/dL solution concentration. The minimal volume variation during titration was achieved by the addition of microliter aliquots of the titrant.

The potentiometric titration of poly(carboxybetaine)s was conducted to determine the apparent pK\textsubscript{a} values, hence the basicity of the COO\textsuperscript{-} conjugate base. The pK\textsubscript{a} values can be calculated from the modified Henderson-Hasselbach eqn (4):

\[ pK_a = pH - n \log \frac{1 - \alpha}{\alpha} \]  

where \( \alpha \) is the protonation degree due to the ratio: 
\[ [ZH^+]_{eq}/[Z^+]_{i} \]
\( [Z^+]_{i} \) is the initial analytical concentration of carboxybetaine repeat unit and 
\([ZH^+]_{eq}\) is the concentration of protonated units at equilibrium given by the relation:

\[ [ZH^+]_{eq} = [C_{H^+}] - [H^+] + [OH^-] \]

where \([C_{H^+}]\) is the concentration of added HCl, and 
\([H^+]\) and \([OH^-]\) were calculated from pH value.

**RESULTS AND DISCUSSION**

**Viscometric Behaviours**

PNVIB-1 does not dissolve in pure water and alcohols, but it is soluble in aqueous solutions of NaCl and CaCl\textsubscript{2}. The insolubility in salt free water may be explained by the chemical structure of PNVIB-1. In water the PNVIB-1 molecules assume a collapsed conformation due to the strong interchain and intra-group associations resulting from the electrostatic attractive forces between the opposite charges of the zwitterionic moieties. These associations prevent PNVIB-1 from dissolving in water. Upon addition of salt, however, these associations are disrupted and the macromolecule assumes an expanded conformation thereby going into solution.

The viscometric behaviours of PNVIB-1 in 0.05 and 0.5 M aqueous solutions of NaCl and CaCl\textsubscript{2} are plotted in Figure 2.

From this figure, on the one hand, one can observe that PNVIB-1 possesses a typical polyzwitterionic behaviour, when its viscosity increases with the increased salt concentration. On the other hand, PNVIB-1 exhibits a behaviour of hard-sphere suspensions in the four solvents, i.e., the reduced viscosity values are insensitive to the polymer concentration.

Table 1 lists the intrinsic viscosity, \([\eta]\), values of PNVIB-1 determined using Einstein-Simha and Rao equations.

The data presented in Table 1 are in good agreement with \([\eta]\) values calculated by these two equations and the enhancement of \([\eta]\) as a function of salt concentration increases. The lowest
[\eta] values are obtained when CaCl₂ was used as a solvent. This first aspect indicates to increased chain expansion as a result of columbic interaction between the charge of the polymer and the added ions. This type of behaviour has been characterized as "anti-polyelectrolyte" behaviour. The second aspect is not a surprise because it is well known that the COO⁻ groups have a higher affinity for Ca²⁺ cation in comparison with the Na⁺ cation, leading to a stronger binding of CaCl₂ than NaCl by PNVIB-1. Thus, this polymer is more collapsed in CaCl₂ aqueous solution. The higher collapsed conformation in CaCl₂ relative to NaCl is due to the bivalent ions Ca²⁺ that can form intra- and interchain bonds between COO⁻ groups.

Figures 3 and 4 illustrate the viscometric behaviours of the PNVIB-2 and PNVIB-3 in water and various alcohols, respectively.

The shape of the plots from Figure 3 shows that:

(i) PNVIB-3 exhibits polyelectrolyte behaviour due to the protonation of the carboxylate groups leading to the corresponding cationic polyelectrolyte; (ii) PNVIB-2 exhibits both a linear dependence of (\eta_{sp}/c) against c and an insensitivity of this viscosity with respect to the variation of concentration of the polymer solution.

It should be mentioned that, from steric point of view the flatness of the internal salt inner structure of PNVIB-3 is more difficult to achieve than in the case of PNVIB-2 because of the CH₃ groups belonging to spacer and therefore, the solubility of PNVIB-3 in water will take place more easily than in the case of PNVIB-2.

From the plots of Figure 4 one can see that PNVIB-3 exhibits the polyelectrolyte behaviour in both alcohols as in water. It was observed that the decreases in reduced viscosity values are related with

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>[\eta]_{Einstein-Simha} (dL/g)</th>
<th>R²_{Einstein-Simha}</th>
<th>[\eta]_{Rao} (dL/g)</th>
<th>R²_{Rao}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNVIB-1</td>
<td>NaCl 0.05 M</td>
<td>0.619</td>
<td>0.998</td>
<td>0.607</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>NaCl 0.5 M</td>
<td>0.890</td>
<td>0.998</td>
<td>0.886</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>CaCl₂ 0.05 M</td>
<td>0.499</td>
<td>0.998</td>
<td>0.494</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>CaCl₂ 0.5 M</td>
<td>0.688</td>
<td>0.998</td>
<td>0.699</td>
<td>0.999</td>
</tr>
</tbody>
</table>

*R²: correlation coefficient

Table 1. Intrinsic viscosity values of PNVI-1 obtained by Einstein-Simha and Rao equations.
the decreases in dielectric constants of solvents: $\text{H}_2\text{O} > \text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH}$. An interesting situation is due by PNVIB-2 sample which exhibits typical polyzwitterionic behaviour in water while in methanol polyelectrolyte behaviour occurs. This situation appears because methanol is a better thermodynamic solvent than water for PNVIB-2. This result was obtained by light-scattering measurements and was reported in our previous study. From the high $M_w$ value (942,200 g/mol) together with a very low $A_2$ value of $0.6798 \times 10^{-7}$ mol.dm$^3$/g$^2$ for PNVIB-2 we assumed that this polymer in distilled water exists as aggregations of polymer chains with spherical conformations. The methanol can be considered the best thermodynamic solvent because PNVIB-2 dissolved in this solvent has the lowest value of $M_w = 246,400$ g/mol and highest value of $A_2 = 5.808 \times 10^{-7}$ mol.dm$^3$/g$^2$. In methanol the dissociation of the interchain aggregations occurs, as well as the shifting of the individual polymer chains to the corresponding cationic polyelectrolyte due to the protonation of COO$^-$ groups by CH$_3$OH [11].

Viscometric data for PNVIB-2 and PNVIB-3 in alcohols were analyzed by Rao and Fuoss equations and led to the $[\eta]$ values given in Table 2.

In the case of PNVIB-3, there are significant differences between the $[\eta]$ values obtained by Rao and Fuoss methods, especially when double distilled water was used as solvent. In methanol, PNVIB-2 behaves as a polyelectrolyte and therefore, Fuoss and Rao equations lead to different values for $[\eta]$. The Rao equation has been applied for the first time for the viscosity of the neutral polymer solutions of dilute to moderate concentrations [16] and later for the polyelectrolytes [17]. The observation that the intrinsic viscosity increases with the solvent dielectric constant

Table 2. Intrinsic viscosity values of PNVIB-2 and PNVIB-3 obtained by Fuoss and Rao equations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>$[\eta]_{\text{Fuoss}}$ (dL/g)</th>
<th>$R^2_{\text{Fuoss}*}$</th>
<th>$[\eta]_{\text{Rao}}$ (dL/g)</th>
<th>$R^2_{\text{Rao}*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNVIB-2</td>
<td>CH$_3$OH</td>
<td>3.579</td>
<td>0.989</td>
<td>2.103</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>16.992</td>
<td>0.987</td>
<td>4.679</td>
<td>0.999</td>
</tr>
<tr>
<td>PNVIB-3</td>
<td>CH$_3$OH</td>
<td>3.310</td>
<td>0.989</td>
<td>2.500</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_5$OH</td>
<td>2.373</td>
<td>0.989</td>
<td>1.905</td>
<td>0.999</td>
</tr>
</tbody>
</table>

$R^2$: correlation coefficient

Figure 5. Representation of Einstein-Simha equation for PNVIB-2.

Figure 6. Representation of Rao equation for PNVIB-2.
leads to an acceptable assumption, namely that the electrolytic dissociation is promoted by polar solvents.

For the PNVIB-2 dissolved in water and in 0.05 and 0.5 M aqueous solutions of NaCl, the $[\eta]$ values were determined using Einstein-Simha and Rao equations.

Figures 5 and 6 present the plots from the Einstein-Simha and Rao equations for PNVIB-2.

From Figures 5 and 6 one can assert that the PNVIB-2 exhibits typical polyzwitterionic behaviour in water and the application of Einstein-Simha and Rao equations leads to very close values of $[\eta]$.

**Potentiometric Titrations**

The potentiometric titrations of poly(carboxybetaine)s led to the following observations: (i) the PNVIB-2 and PNVIB-3 aqueous solutions displayed the same behaviour during the potentiometric titrations with 0.5 M HCl solution; (ii) when PNVIB-2 and PNVIB-3 were dissolved in 0.5 M NaCl solution, for the same HCl amount added, the higher pH values of salt solutions of poly(carboxybetaine) are observed compared with their aqueous solutions.

Table 3 lists the pK$_a$ and n values of PNVIB-1 determined using Henderson-Hasselbach equation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>pK$_a$</th>
<th>n</th>
<th>$[\eta]_{Rao}$ (dL/g)</th>
<th>R$^2*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNVIB-1</td>
<td>NaCl 0.5 M</td>
<td>2.254</td>
<td>2.254</td>
<td>1.36</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>2.586</td>
<td>2.586</td>
<td>1.25</td>
<td>0.999</td>
</tr>
<tr>
<td>PNVIB-2</td>
<td>NaCl 0.5 M</td>
<td>3.746</td>
<td>3.746</td>
<td>1.79</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>2.970</td>
<td>2.970</td>
<td>1.19</td>
<td>0.998</td>
</tr>
<tr>
<td>PNVIB-3</td>
<td>NaCl 0.5 M</td>
<td>4.435</td>
<td>4.435</td>
<td>1.83</td>
<td>0.998</td>
</tr>
</tbody>
</table>

$^*$R$^2$: correlation coefficient

**CONCLUSION**

The studied poly(carboxybetaine)s based on PNVI exhibited different behaviours towards water, methanol and ethanol used as solvents. Thus, poly(carboxybetaine) with one methylene group between N$^+$ and COO$^-$ groups was insoluble in all solvents, only the addition of salts into water led to its dissolution. This situation is due to the fact that this polymer forms an interchain ionic network and the addition of electrolytes breaks this network leading to the dissolution of the polymer. The viscometric behaviour of this poly(carboxybetaine) is "antipolyelectrolyte", i.e., the reduced viscosity values increase with increased salt concentration. The conformations of the polymer chains are of hard-spheres because the reduced viscosity values are insensitive to the polymer concentration. The viscometric experimental data for this polymer dissolved into 0.05 and 0.5 M NaCl and CaCl$_2$ aqueous solutions were plotted based on Einstein-Simha and Rao equation terms when very close values for the intrinsic viscosity, $[\eta]$, were obtained.

Poly(carboxybetaine) with two methylene groups between quaternary nitrogen atoms and carboxylate groups was soluble both in water and methanol. This solubility is due to the possibility of an inner-salt structure which yielded to the neutralization between N$^+$ and COO$^-$ in the same betaine unit through very stable five membered cycles. In water this structure is stronger than in methanol because water is a poorer solvent for this poly(carboxybetaine). The viscometric behaviours are strongly dependent on the nature of...
solvent. Thus, in aqueous solution this polymer exhibited an anti-polyelectrolyte behaviour while in methanol it is a polyelectrolyte. The values for $[\eta]$ were assessed by Einstein-Simha and Rao equations when the polymer was dissolved in aqueous salt solutions and by Fuoss and Rao equations for methanol. Both equations can be applied for the aqueous solution in order to assess the $[\eta]$ because they lead to similar values. In the case of methanol, when PNVIB-2 displayed polyelectrolyte behaviour, the Fuoss and Rao equations led to different values.

Poly(carboxybetaine) with a side -CH$_3$ group at the spacer between N$^+$ and COO$^-$ groups is soluble both in water and the two alcohols. This polymer exhibited polyelectrolyte behaviour in the investigated solvents. In this case, the five-membered cycles exhibit, probably, a high instability due to the -CH$_3$ side group from the spacer, leading to the protonation of the COO$^-$ group both in water and alcohols. The $[\eta]$ values were determined using the Fuoss and Rao equations, but the different values were obtained.

The apparent pK$_a$ values obtained by potentiometric titrations of poly(carboxybetaine)s with 0.5 M HCl, are strongly dependent of solvent nature. Thus, the PNVIB-2 and PNVIB-3 have lower apparent pK$_a$ values in deionized water than in 0.5 M NaCl. Therefore, the basicity of COO$^-$ conjugate base is lower in the first solvent than in the second solvent.

REFERENCES

