# Some poly(carboxybetaines) and their solution properties

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A study on the viscometric behaviour of the three poly(carboxybetaines) based on poly(N-vinylimidazole) was performed. These poly(carboxybetaines) possess a space of one, two and three carbon atoms between quaternary ammonium group and carboxylate one, the last poly(carboxybetaine) containing the spacer with a side $–CH_3$ group. From the study achieved was observed that poly(carboxybetaines) with one methylene group between the two oppositely charged groups is insoluble in water but it is soluble in saline media and exhibit an antipolyelectrolyte behaviour namely an increase of the viscosity with increasing salt concentration. The poly(carboxybetaine) with two methylene group between $N^+$ and $COO^-$ is soluble both in water and aqueous salt solutions and with a mixed viscosimetric behaviour. Thus, the addition of salt (i.e., NaCl, $CaCl_2$) leads to the decrease of the intrinsic viscosity but this decrease is greater in salt solutions of lower concentration. In contrast to the first two poly(carboxybetaine), that with three carbon atoms between $N^+$ and $COO^-$ has a clearly polyelectrolyte behaviour.

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## 1. Introduction

Poly(carboxybetaines) are an important class of poly(zwitterionic) polymers. These polymers (PZs) unlike polyelectrolytes (PEs) which bear either anionic or cationic chargers, bear both anionic and cationic groups on the same chain.

Poly(betaines) (PBs) divided in poly(sulfobetaines), poly(carboxybetaines) and poly(phosphobetaines) contain the two oppositely charged groups in the same structural unit of polymeric chain with a quaternary ammonium group as positive group that is not adjacent the negative one (carboxylate, sulfonate and phosphonate, respectively).

Because of high dipolar character, PBs exhibit markedly different behaviours than PEs in aqueous solutions [1-8]. Thus, PEs usually exhibit decreases in the hydrodynamic volume and solution viscosity upon the additions of low molecular mass electrolytes, while PBs tend to the increases of the solution viscosities with increasing added salt concentration, so-called "antipolyelectrolyte effect".

Also, a difference between PEs and PBs appears in the solid state. Thus, a PE in the mixture with a salt gives only an ion-exchange between its contraions and the ion of the same sign of salt while a PB forms homogenous blends when is mixed with some inorganic salts in equimolecular amounts.

Solution and solid state properties of PBs are governed by many factors including the charge density, charge asymmetry, molecular mass and the distance between the two oppositely charged groups, so-called "spacer".

Because of above-mentioned special properties, PBs are polymers with growing scientific and commercial interest. Thus, these polymers have a structural similarity with peptides and living matters serving as models for them 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 this paper is the study of the solution properties of some poly(carboxybetaines) based on poly(N-vinylimidazole) namely the viscometric behaviours of the aqueous solutions with and without added salts of the poly(carboxybetaines) which contain structural units of [1-vinyl-3-(1-carboxymethyl) imidazolium betaine]; [1-vinyl-3-(2-carboxyethyl) imidazolium betaine] and [1-vinyl-3-(2-carboxy-isoprpyl) imidazolium betaine].

## 2. Experimental

The synthesis of the poly(carboxybetaines) was previously shown [9-12].

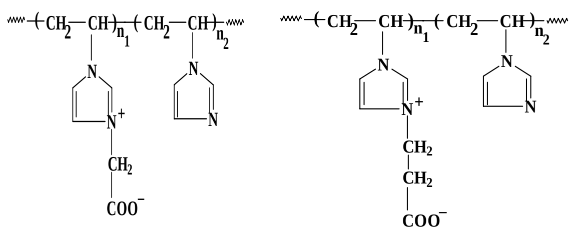
Viscosity measurements

Solution viscosities were determined with an Ubbelohde viscometer at different temperature, water flow time at 25 $^0$C being 168 s.

Stock solutions of the salts were prepared by dissolving the appropriate salt amount in bidistilleted water. The poly(carboxybetaines) were dissolved in water or in the salt solutions to yield 0.5 % (g/dL) stock solutions. These solutions were subsequently diluted with water or the appropriate salt solution.

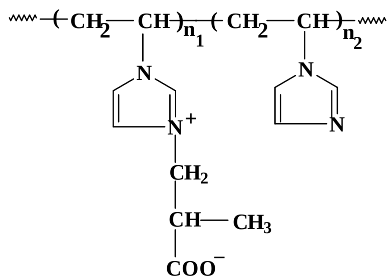
## 3. Results and discussion

The chemical structures of the three poly(carboxybetaines) performed for this study are shown in Scheme 1.



**PNVIB-1**
**$n_1$ = 94 %**

**PNVIB-2**
**$n_1$ = 96 %**



**PNVIB-3**
**$n_1$ = 87 %**

*Scheme 1- Poly(carboxybetaines) based on poly(N-vinylimidazole).*

It should be mentioned that PNVIB-1 is not soluble in water without added salts while PNVIB-2 and PNVIB-3 are soluble both in water and aqueous salt solutions (i.e., NaCl and $CaCl_2$).

In the Fig. 1 are showed the dependence of the reduced viscosities of polymer concentration for PNVIB-1 when this polymer is dissolved into NaCl and $CaCl_2$ aqueous solutions.

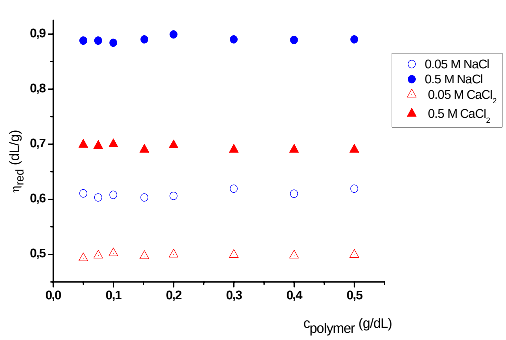



*Fig. 1. The reduced viscosity as a function of PNVIB-1 concentration in aqueous solutions of NaCl and $CaCl_2$, at 25 $^0$C.*

All the plots from Figure 1 show that reduced viscosities are insensitive to the polymer concentration. This behaviour is typical for hard-sphere suspension and for such systems the viscosity data may be analyzed through a modified of the Einstein-Simha equation (1) [13,14] and the corresponding plots are given in Fig. 2.

$$\eta_{rel} = 1 + [\eta]c \qquad (1)$$

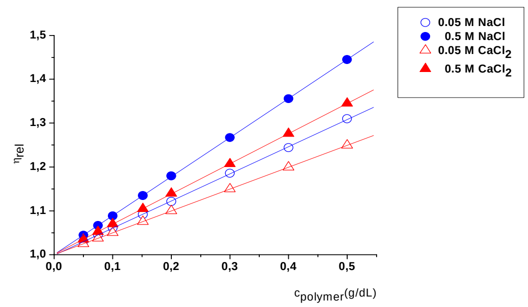



*Fig. 2. Relative viscosities as a function of PNVIB-1 concentration dissolved in NaCl and $CaCl_2$ aqueous solution of different concentration, at 25 $^0$C; correlation coefficient 0.99991 – 1.0.*

The slopes of the plots from Fig. 2 give the intrinsic viscosity values for PNVIB-1 dissolved in the four solvents and they are showed in Table 1.

*Table 1. Variation of the intrinsic viscosity of PNVIB-1 as a function of solvent nature.*

| Solvent | [η] dL $g^{-1}$ |
|---|---|
| NaCl 0.05M | 0.6193 |
| NaCl 0.5 M | 0.8900 |
| $CaCl_2$ 0.05 M | 0.4988 |
| $CaCl_2$ 0.5 M | 0.6883 |

The dependence of the intrinsic viscosity on the nature of the added ions reflects the site-binding of the salt ions to the zwitterionic groups.

The data of Table 1 show an enhancement of the [η] as the salt concentration is increased and in the case of the same salt concentration, PNVIB-1 has the higher [η] when it is dissolved in NaCl aqueous solution.

This first aspect shows clearly an antipolyelectrolyte behaviour of PNVIB-1 and the last aspect is in contrast to poly(sulfobetaines) when [η] has higher values in $CaCl_2$ (chlorhide with divalent cation) than in NaCl [15].

This finding is not a surprise because it is well known the higher affinity of $COO^-$ groups for Ca(II) cation in comparison with that of $Na^+$ cation leading to a stronger binding of $CaCl_2$ by PNVIB-1 than of NaCl. Thus, in the $CaCl_2$ aqueous solution this polymer should be more collapsed, therefore with lower [η] values than in NaCl aqueous solutions.

Fig. 3 shows the viscometric behaviour of PNVIB-2 solutions in different solvents.

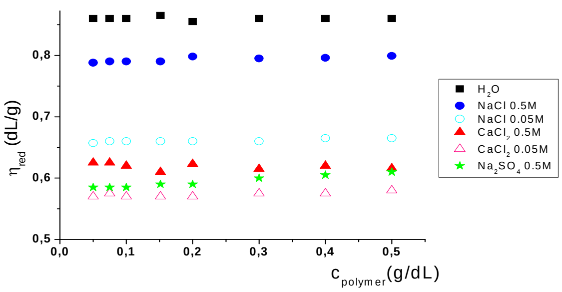



*Fig. 3. The dependence of the reduced viscosities on polymer concentration for PNVIB-2.*

From the plots of the Fig. 3 can be observed that in the presence of salts PNVIB-1 and PNVIB-2 have the same behaviour.

Viscometric data for PNVIB-2 analyzed by Einstein-Simha equation led to the [η] values given in Table 2.

*Table 2. Variation of the intrinsic viscosity of PNVIB-2 as a function of solvent nature*

| Solvent | [η] (dL $g^{-1}$) | R* |
|---|---|---|
| $H_2O$ | 0.8689 | 0.999 |
| 0.05 M NaCl | 0.6672 | 0.999 |
| 0.5 M NaCl | 0.8002 | 0.999 |
| 0.05 M $CaCl_2$ | 0.5822 | 0.999 |
| 0.5 M $CaCl_2$ | 0,6135 | 0.998 |
| 0.5 M $Na_2SO_4$ | 0.6097 | 0.999 |

*R = correlation coefficient

From the Table 2 can be mentioned the following aspects: the [η] values increase with increasing salt concentration, the salts which contain divalent ions determine the lower [η] and in the water is observed the highest [η] value.

The highest [η] value of PNVIB-2 aqueous solution without added salts is, probably, due to the fact that in pure water the zwitterionic polymer chains can exist as a mixture of interchain aggregates and individual chains because of the dipole-dipole interaction between zwitterionic groups [16]. The addition of small amount of electrolytes leads to the breakup of the inter- and intrachain associations, therefore to the decrease of [η] while the higher salt amounts determines the individual polymeric chain extension and the [η] increase as well.

In order to evidence the temperature influence on the solution viscosity of poly(carboxybetaine), the viscometric behaviours of PNVIB-2 dissolved in water as well as 0.5 M NaCl and $CaCl_2$ in the 25 – 55 $^0$C temperature domain were analyzed.

Fig. 4 shows the effect of temperature on the intrinsic viscosities determined from Einstein – Simha plots.

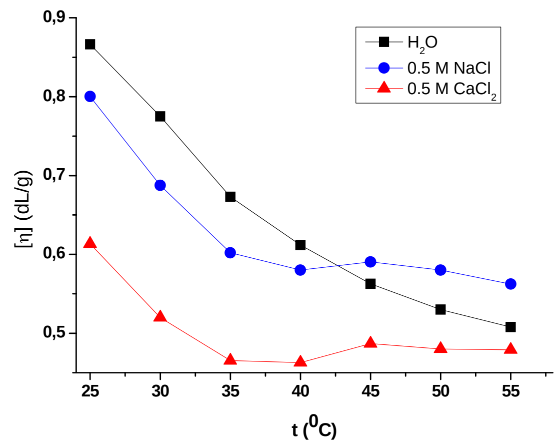



*Fig. 4. Intrinsic viscosities as a function of temperature and the solvent nature.*

An examination of Fig. 4 reveals a continous decrease of [η] with increasing temperature when PNVIB-2 is dissolved in water while PNVIB-2 dissolved in 0.5 M NaCl and $CaCl_2$ exhibit a mixed behaviour as a function of temperature. Thus, at 35 $^0$C a minimum and at 45 $^o$C a maximum are observed.

This finding is in contrast to the influence of the temperature on PE solution viscosity where a continuous increase of the viscosity occurs with increasing temperature.

The viscosimetric behaviours of PNVIB-3 in water with and without added salts (NaCl and $CaCl_2$) are shown in Fig. 5 and 6 where the variation of the reduced viscosity as a function of polymer concentration is plotted.

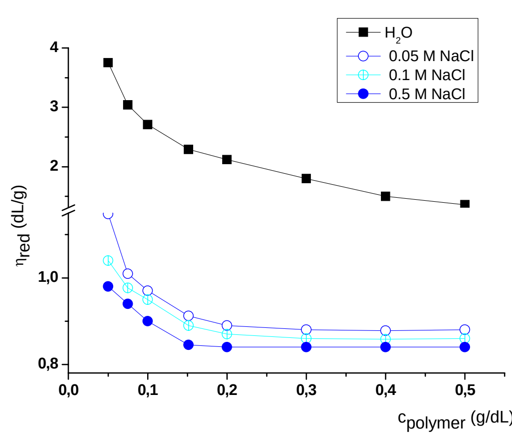



*Fig. 5. The reduced viscosity of the PNVIB-3 as a function of polymer concentration in water and NaCl aqueous solutions of various concentrations, at 25 $^o$C*

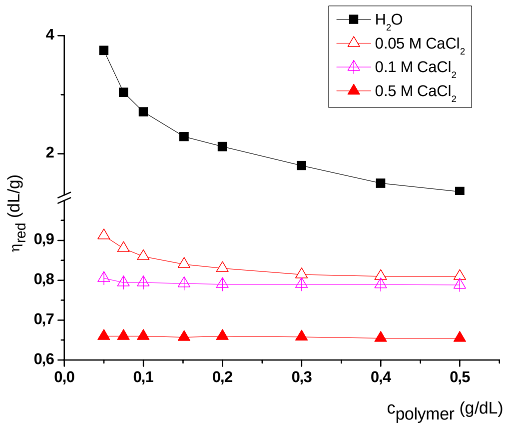



*Fig. 6. The reduced viscosity of the PNVIB-3 as a function of polymer concentration in $CaCl_2$ aqueous solution of various concentrations, at 25 $^0$C*

The plots from Fig. 5 and 6 show a polyelectrolyte behaviour of PNVIB-3 namely in water a non-linear dependence of the reduced viscosity of polymer concentration with an increase of $\eta_{red}$ as the polymer concentration decreases and a continuous decrease of $\eta_{red}$ with increasing added salt amount.

## 4. Conclusions

The study provides informations about the viscometric behavious both in water and saline aqueous media of the three poly(carboxybetaines) based on poly(N-vinylimidazole). These information are both of scientific and commercial interest because it is known that the poly(carboxybetaines) can be used in petroleum production, water treatment and personal care product, where the ionic polymers with saline medium tolerance are required.

Concerning the poly(carboxybetaines) of the present study, PNVIB-1 and PNVIB-2 are indicated for the use in the saline media because of their [η] increase with increasing salt concentration.

## References

[1] F. Candau, J. F. Joanny, In Polymeric Materials Encyclopedia, Ed. J. C. Salamone, CRC Press: Boca Raton, FL, 1996, Vol. 7, p 5476.
[2] S. E. Kudaibergenov, Polyampholytes: Synthesis, Characterization and Application; Plenum: New York (2002).
[3] E. A. Bekturov, S. E. Kudaibergenov, Makromol Chem Macromol Symp **26**, 281 (1989).
[4] E. A. Bekturov, S. E. Kudaibergenov, S. R. Rafikov, J Macromol Sci Rev Macromol Chem Phyls **30**, 233 (1990).
[5] P. G. Higgs, J. F. Johanny, J Chem Phys **94**, 1543 (1991).
[6] Y. Kantor, H. Li, M. Kardar, Phys Rev Lett **69**, 61 (1992).
[7] A. V. Dobrynin, M. Rubinstein, J Phys II **5**, 677 (1995).
[8] S. E. Kudaibergenov, Adv Polym Sci **144**, 115 (1999).
[9] V. Bărboiu, E. Streba, C. Luca, C. I. Simionescu, J.Polym. Sci.: Part A: Polym. Chem. **33**, 389 (1995).
[10] C. Luca, E. Streba, V. Bărboiu, Progress in Ionic Exchange, Advances and Applications, Eds. A. Dyer, M. J. Hudson, P. A. Williams, The Royal Society of Chemistry, 1995, p. 78.
[11] V. Bărboiu, E. Streba, M. N. Holerca, C. Luca, J. M. S. Pure Appl. Chem. **A32**, 1385 (1995).
[12] C. Luca, V. Neagu, S. Vasiliu and V.Barboi, In Focus on Ionic Polymers, Ed. E. S. Dragan, Research Singpost, Kerala, India, 2005, p. 117.
[13] J. C. Salamone, C. C. Tsai, A. P. Olson, A. C. Watterson, Ions in polymers, Ch. 22. Advances in Chemistry Series No. 187. Washington DC: American Chemical Society (1980).
[14] S. A. Fzzell, C. L. McCormick, Macromolecules **25**, 1881 (1992).
[15] I. V. Berlinova, I. V. Dimitrov, R. G. Kalinova, N. G. Kalinova, N. G. Vladimirov, Polymer **41**, 831 (2000).
[16] A. Niu, D. J. Liaw, H. C. Sang, C. Wu, Macromolecules **33**, 3492 (2000).

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