



Dedicated to Professor Bogdan C. Simionescu  
on the occasion of his 65<sup>th</sup> anniversary

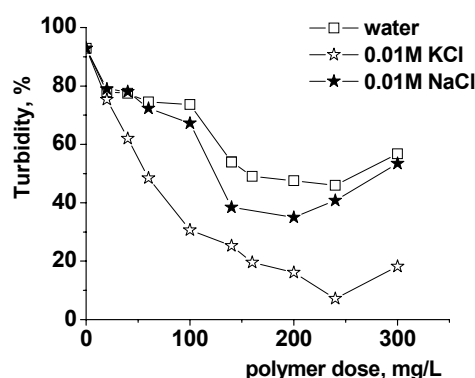
## PEG IN AQUEOUS SALT SOLUTIONS. VISCOSITY AND SEPARATION ABILITY IN A TiO<sub>2</sub> SUSPENSION

Cristina-Eliza BRUNCHI\* and Luminita GHIMICI

"Petru Poni" Institute of Macromolecular Chemistry,  
41-A Grigore Ghica Voda Alley, 700487 Iași, Roumania

Received October 1, 2012

The hydrodynamic and separation properties of poly(ethylene glycol) (PEG) in aqueous salt solution at room temperature were investigated as a function of polymer concentration as well as salt nature and concentration. The viscometric data are discussed in terms of the macromolecular coils dimensions. The intrinsic viscosities were determined by means of the Wolf method. The results show that the experimental data fit well with the Wolf model. The separation process was investigated by turbidity measurements in a titanium dioxide suspension. A good separation performance was observed for salt solutions of PEG.



### INTRODUCTION

Poly(ethylene glycol) is a water-soluble neutral polymer which exhibits an unusual behavior in aqueous solutions, *i.e.*, unlike other neutral polymers, its solubility decreases with temperature and phase separation occurs above a critical temperature that depends on the molecular weight.<sup>1,2</sup> This behavior is determined by the competition of PEG and water as proton acceptors in hydrogen bonding formation (water-PEG and water-water hydrogen bonding); at higher temperatures there is a decrease in number of hydrogen bonds and an increase of hydrophobic interactions between the macromolecular chains.<sup>3</sup>

Addition of electrolytes into aqueous PEG solutions leads also to the decrease of PEG solubility with disrupting ethylene glycol-water structure by salting-out effect and/or by complexation of PEG with cations.<sup>4</sup> The understanding of the complex behavior of PEG in aqueous solution both in the presence and absence of salts as well as of its unique properties (lack toxicity, biocompatibility, absence of antigenicity and immunogenicity, ability to inhibit protein adsorption, to replace some biopolymers, and to form various aggregates in water<sup>5</sup>) is essential for particular applications in industry, medicine, pharmacy, food, environment, etc.

\* Corresponding author: [brunchic@icmpp.ro](mailto:brunchic@icmpp.ro)

One of the most used methods to assess the behavior of polymer in solutions is the viscometric one. By processing the viscometric data one could obtain information about some hydrodynamic parameters (the intrinsic viscosity,  $[\eta]$ , characteristic specific hydrodynamic volume,  $[\eta]^\bullet$ , specific hydrodynamic volume at a given polymer concentration,  $\{\eta\}$ , etc.), polymer-polymer interactions, excluded volume effects governed by polymer-solvent interactions and chain stiffness.

Regarding the intrinsic viscosity, it is well known that for dilute neutral polymer solution it can be obtained by means of the Huggins equation (1).

$$\frac{\eta_{sp}}{c} = [\eta]_H + k_H [\eta]_H^2 c \quad (1)$$

where:  $\eta_{sp}$  represents the specific viscosity ( $\eta_{sp} = \eta_r - 1$ ), which reflects the fractional change in viscosity produced by the addition of the solute,  $\eta_r$  is the relative viscosity showing the change in viscosity, usually expressed as a ratio between the viscosity of the polymer solution and the viscosity of the solvent,  $[\eta]_H$  is the intrinsic viscosity determined by Huggins method,  $k_H$  represents the Huggins constant which offers information about the polymer interactions and the solvent quality, and  $c$  is the polymer concentration in solution.

Unlike uncharged polymers, the solutions of ionic polymers show a different viscometric behavior which consists in the continuously increase of the reduced viscosity with dilution over a wide concentration range. Due to the concave upward of  $(\eta_{sp}/c) - c$  curve the above mentioned equation cannot be straightly applied to obtain  $[\eta]$ . Even if there are a large number of studies in finding an equation to allow assessment of intrinsic viscosity of polyelectrolyte in solution,<sup>6-8</sup> it is still difficult to find equations that depict their viscosity behavior in the whole range of concentration. Quite recently, a purely phenomenological approach for determination of  $[\eta]$  has been presented by Wolf.<sup>9</sup> In this method  $[\eta]$  can be determined from initial slope of dependence of  $\ln \eta_r$  as a function of  $c$  at sufficiently low shear rates and polymer solution concentration, according to the following equation:

$$\ln \eta_r = \frac{c[\eta] + bc^2[\eta][\eta]^\bullet}{1 + bc[\eta]} \quad (2)$$

where:  $[\eta]$  is the intrinsic viscosity determined by the Wolf method,  $b$  represents a viscometric interaction parameter and  $[\eta]^\bullet$  is the characteristic specific hydrodynamic volume which incorporate the effects of electrostatic interactions.

The values of intrinsic viscosity,  $[\eta]$ , as well as the values of  $[\eta]^\bullet$  and  $b$  constants can be determined by fitting experimental data using eq. 2.

Being initially developed for the evaluation of the intrinsic viscosity of polyelectrolyte in aqueous solutions in the presence/absence of the salt,<sup>10-12</sup> it has been further successfully applied for polyelectrolyte in aqueous/organic solvent mixtures<sup>13,14</sup> and for neutral (co)polymers, neutral polymer mixtures and neutral polymers in solvents mixture.<sup>15-18</sup>

The goal of the present work was to describe the viscosity behavior of PEG in water and aqueous salt solutions (NaCl and KCl) in terms of the Wolf method. Hitherto, as far as we could ascertain, there is no data regarding the use of the Wolf equation for intrinsic viscosity determination in the case of PEG.

The separation of TiO<sub>2</sub> suspension in the presence of aqueous solutions, with or without salts, of PEG was also discussed and related with the viscometric data.

## RESULTS AND DISCUSSIONS

### Viscometric study

The analysis of the Fig. 1a and 1b which depict the  $(\eta_{sp}/c) - c$  plots for aqueous solution of PEG both in water and water containing salts (NaCl and KCl) reveals the following aspects: i) a linear decrease of the reduced viscosity values with dilution like the neutral polymers in water and aqueous salt solutions with  $c_s \geq 1M$  ( $c_s$  = salt concentration); ii) a slight polyelectrolyte effect, *i.e.*, an upward curvature appeared at high dilution for PEG in aqueous salt solution with  $c_s < 1M$ ; the polyelectrolyte behavior is determined, as it was already shown in other investigations, by the presence of the oxygen atoms in the ethylene oxide units which can bind cations leading to the charging of the polymer chains.<sup>10,11,13</sup> The electrostatic repulsive forces between the charged groups lead to the chain expansion and thus, the reduced viscosity increases with dilution. Further increase of the salt concentration (at fixed polymer

concentration) should increase the number of adsorbed cations on the chain, and hence, the increase of the solution viscosity. This effect is partly counterbalanced by the charge screening which appears at high ionic strength ( $c_s \geq 1\text{M}$ ); the charges on the chain are neutralized and the reduced viscosity decreases.

As mentioned in Introduction, the Huggins method cannot be used for determination of intrinsic viscosity in the case of polyelectrolytes. Therefore, in order to obtain this hydrodynamic parameter we applied the Wolf equation (eq.2) to the viscosity data obtained both in water and water containing salts (Fig. 2a and 2b).

The results demonstrate that all of the calculated curves (lines) coincided well with the

experimental points and confirm that the eq.2 is appropriate to describe the viscosity behavior of PEG in all investigated systems. All the intrinsic viscosities values are included in Table 1.

The slightly higher values of the intrinsic viscosity recorded for PEG in KCl than NaCl solutions could be explained by the well known higher affinity of this polymer for  $\text{K}^+$  than  $\text{Na}^+$ .<sup>19</sup> According to the Wolf method, for solutions where PEG had a neutral polymer behavior,  $[\eta]^*$  was zero. Also, the positive values of the viscometric interaction parameter,  $b$ , means a good solvent for polymer, while the negative ones indicate unfavorable polymer – solvent interactions.

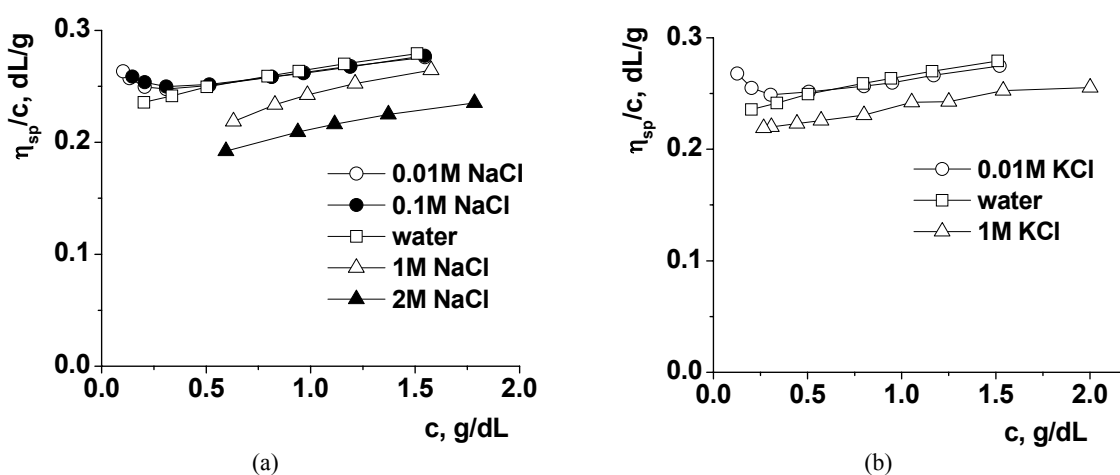


Fig. 1 – Reduced viscosity,  $\eta_{sp} / c$ , dependence on the polymer concentration,  $c$ , in water and aqueous salt solutions NaCl (a) and KCl (b).

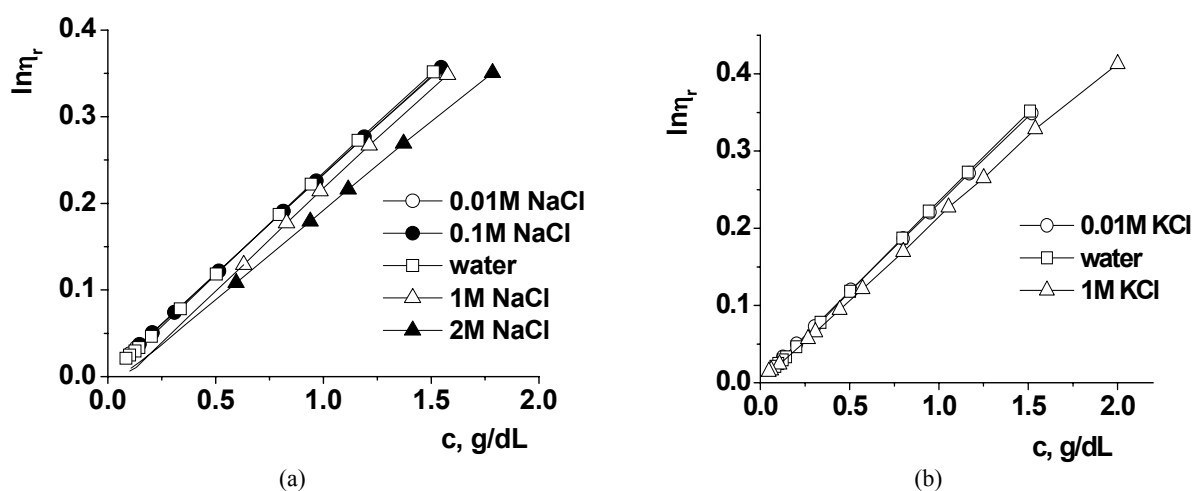


Fig. 2 – Relative viscosity,  $\ln \eta_r$ , dependence on the polymer concentration,  $c$ , in water and in aqueous salt solutions NaCl (a) and KCl (b).

Table 1

Viscometric parameters determined by Wolf method and the correlation coefficients of fits (as  $r^2$ ) for PEG in water and aqueous salt solutions

Nr. Crt Solvent	$[\eta]$ , dL/g	$b$	$[\eta]^*$	$r^2$
1. Water	0.2367	0.039	0	0.9998
2. NaCl				
0.01M	0.2405	0.2824	0.1377	0.9998
0.1M	0.2403	-0.0969	0.5056	0.9998
1M	0.2021	-0.2901	0	0.9993
2M	0.1844	-0.2005	0	0.9996
3. KCl				
0.01M	0.2411	0.1520	0.0151	0.9998
1M	0.2195	0.1282	0	0.9996

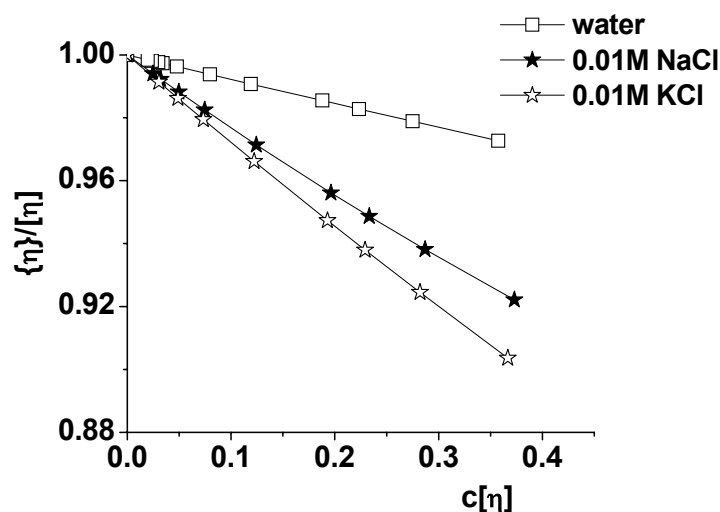


Fig. 3 – Reduced specific hydrodynamic volume,  $\{\eta\}/[\eta]$  dependence on the reduced polymer concentration,  $c[\eta]$ , for PEG in water and aqueous salt solutions with  $c_s = 0.01M$ .

For a deeper understanding of the viscometric behavior, Wolf introduced another hydrodynamic parameter: the specific hydrodynamic volume at a given polymer concentration,  $\{\eta\}$ . The ratio between the specific hydrodynamic volume at a given polymer concentration and that at infinite dilution,  $\{\eta\}/[\eta]$ , provides information on the changes in the hydrodynamic volume of an individual macromolecule induced by the presence of other macromolecules. The value of this ratio can be obtained from the following equation:

$$\frac{\{\eta\}}{[\eta]} = \frac{1 + 2rb(c[\eta]) + rb^2(c[\eta])^2}{1 + 2b(c[\eta]) + b^2(c[\eta])^2} \quad (3)$$

where:  $r = [\eta]^*/[\eta]$  and  $c[\eta]$  is dimensionless of reduced concentration.

For uncharged polymers  $[\eta]^* = 0$  and eq.3 is reduced to:

$$\frac{\{\eta\}}{[\eta]} = \frac{1}{1 + 2b(c[\eta]) + b^2(c[\eta])^2} \quad (4)$$

Fig. 3 shows the dependence  $\{\eta\}/[\eta]$  vs the reduced concentration for PEG in water and 0.01M salt solutions; the parameters  $[\eta]$ ,  $[\eta]^*$  and  $b$  in eqs.3 and 4 were taken from Table 1. The decrease of  $\{\eta\}/[\eta]$  from 1 ( $\{\eta\}/[\eta] = 1$  at  $c[\eta] = 0$ ), as

$\{\eta\} = [\eta]$ ) with increasing reduced polymer concentration was observed for PEG solutions both in water and water containing salts over the whole reduced concentration range studied.

For uncharged polymer (the case of PEG in water) as compared with polyelectrolyte (aqueous salt solution of PEG with  $c_s = 0.01\text{M}$ ) the decrease of the  $\{\eta\}/[\eta]$  ratio with increasing of  $c[\eta]$  is smaller, that means a more pronounced shrinking of the macromolecular coils in the latter case.

This is a consequence of the progressive screening of the electrical charges that result from the additional solute molecules. This finding is in agreement with those found for other systems.<sup>10-12</sup>

### Separation study

Another step in our experiments was the investigation of PEG solutions ability in separation of the TiO<sub>2</sub> suspension (Fig. 4). The experiments were performed both in the presence and absence of salts.

The residual turbidity values decrease with increasing polymer dose (the polymer dose means the polymer concentration in its mixture with TiO<sub>2</sub> suspension) reaching a minimum and then increased again for all the investigated systems. Besides the common feature, there are some differences indicating better separation efficiency when PEG was used in salt solutions than in pure water. This behavior can be explained as follows. For effective separation, polymers need to be adsorbed on particles. According to the literature data, PEG can interact with oxide particles in suspension, mainly,

through hydrogen bonding established between the ether oxygen of polymers and OH groups on the particles surface.<sup>20,21</sup> There are different types of surface groups on titanium dioxide particles ( $-\text{TiOH}_2^+$ ,  $-\text{TiOH}$ ,  $-\text{TiO}^-$ ), their concentrations depending on the pH of the suspension.<sup>22</sup>

Thus, at pH higher than that corresponding to the isoelectric point, the concentrations of  $-\text{TiOH}$  groups and titanium dioxide positively charged ( $-\text{Ti}-\text{OH} + \text{H}^+ \rightarrow -\text{TiOH}_2^+$ ) decrease and that of the oxide negatively charged ( $-\text{Ti}-\text{OH} + \text{OH}^- \rightarrow -\text{TiO}^- + \text{H}_2\text{O}$ ) increases. Taking into consideration that the pH value corresponding to the isoelectric point of the TiO<sub>2</sub> particles under investigation is 2.56 (see the Experimental part) and the natural pH is 6.2, the concentration of the  $-\text{TiO}^-$  groups prevails; the adsorption of polymer samples by hydrogen bonding is not favorable and hence, the bad destabilization ability of PEG in pure water. On the other hand, the more pronounced decrease of the residual turbidity noticed in the presence of 0.01M salt solutions of PEG can be explained by the electrostatic interactions between cations ( $\text{Na}^+$  and  $\text{K}^+$ ) bound at the oxygen atoms of ethylene oxide unit, proved by viscosity measurements (see Fig. 1), and  $\text{TiO}^-$  groups on the particle surface. The higher separation efficiency of PEG in 0.01M KCl solution (minimum residual turbidity below 8 % at a polymer doses of 200-240  $\text{mg L}^{-1}$ ) than 0.01M NaCl (minimum residual turbidity around 35 % at a polymer dose of 200  $\text{mg L}^{-1}$ ) confirms the higher affinity of PEG for  $\text{K}^+$  than  $\text{Na}^+$ , and hence, the increased number of adsorbed  $\text{K}^+$  on the polymer chain.

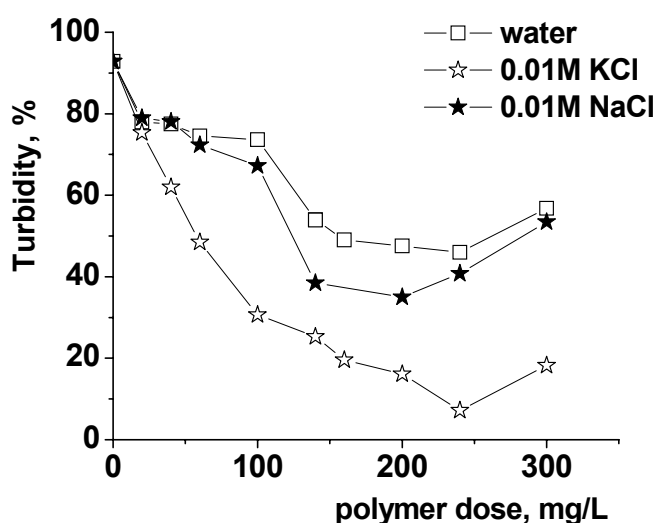


Fig. 4 – Residual turbidity (%) dependence on the polymer dose for PEG in water and water containing salts,  $c_s = 0.01\text{M}$ , settling time: 20 hours.

## EXPERIMENTAL

### Materials

Poly(ethylene glycol) with  $M_v=10,000$  and the salts (NaCl and KCl) were supplied by Sigma-Aldrich. TiO<sub>2</sub> particles, crystalline form anatase, as determined by X-ray analysis (Bruker D8 ADVANCE, Germany) was supplied by Sigma-Aldrich. The hydrodynamic size of the particles, Z-Average (d, nm), determined by DLS measurements, was 401.7. The isoelectric point (IEP), *i.e.*, the pH at which zeta potential vanishes to zero, was found at about 2.56. All compounds were used without further purification.

### Measurements

*Viscometric measurements* of the polymer solutions were carried out at 25 °C with an Ubbelohde suspended-level viscometer with a capillary diameter of 0.64 mm (Type 531 10, Schott-Geräte) in combination with automatic viscometer (Instrument LAUDA LMV 830) with a water bath (ECO ET 155). The time measurement error was 1 ppm and the flow volume of the viscometer was greater than 5 mL, making drainage errors unimportant. Polymers were dissolved in double-distilled water and salt aqueous solutions. The polymer solutions were prepared with one day before the experimental measurements. All viscosity measurements were repeated at least twice in order to check the reliability of the data.

*Separation measurements*: the aqueous polymer solutions (both in the absence and presence of salts) as well as the TiO<sub>2</sub> model dispersions were prepared with distilled water. The concentration of the TiO<sub>2</sub> model dispersions was 0.05 g L<sup>-1</sup>, the initial pH = 6.2 and zeta potential  $\zeta = -38.1$  mV. In order to fully disperse the TiO<sub>2</sub> powder the dispersions were sonicated for 15 min using an ultrasonicator (SONICS VCX 750).

The separation experiments were conducted at room temperature. 50 ml of the TiO<sub>2</sub> suspension were placed into 100 ml glass beakers. Different volumes of polymer solutions were added at 500 rpm and stirring was continued with the same speed for about 3 min and then decreased to about 100 rpm for 15 min. After different settling times the turbidity of the supernatant was measured with a spectrophotometer SPECORD 1300 Analytik Jena at  $\lambda = 400$  nm. A blank experiment was carried out in the absence of polymer to evaluate "natural" sedimentation of the suspensions under the selected experimental conditions (pH, concentration of suspended mater). The TiO<sub>2</sub> suspension was very stable in the absence of polymer as the residual turbidity values did not decrease below 95 % even after 20 hour of settling time. The residual turbidity (%) was expressed as percent of the initial turbidity of the TiO<sub>2</sub> suspensions, at time zero in the absence of polymer. All experiments were performed in triplicate and the mean turbidity values were calculated.

## CONCLUSIONS

The solution properties of PEG were investigated in water and aqueous salt solution (NaCl and KCl) with different concentrations. The variation of the viscosity as a function of polymer concentration in terms of the Huggins method shows an upward curvature at high dilution for

PEG in aqueous salt solutions with  $c_s < 1M$ . This trend is characteristic for polyelectrolyte behavior and for PEG could be ascribe to presence of oxygen atoms in the ethylene oxide units which can bind cations leading to the charging of polymer chains. The viscometric behavior of PEG solutions both in the presence and absence of salts was described by means the Wolf model. A higher separation efficiency of TiO<sub>2</sub> suspension was noticed when PEG in 0.01M KCl solution was used.

*Acknowledgements*: This work was supported by a grant of the Roumanian National Authority for Scientific Research, CNCS-UEFISCDI, and project number PN-II-ID-PCE-2011-3-0199 (contract number 300/2011).

## REFERENCES

1. H. Venohr, V. Fraaije, H. Strunk and W. Borchard, *Eur. Polym. J.*, **1998**, *34*, 723-732.
2. E. E. Dormidontova, *Macromolecules*, **2002**, *35*, 987-1001.
3. C. Özdemir and A. Güner, *J. Appl. Polym. Sci.*, **2006**, *101*, 203-216.
4. R. Heeb, S. Lee, N. V. Venkataraman and N. D. Spencer, *Appl. Mater Interfaces*, **2009**, *1*, 1105-1112.
5. C. Allen, D. Maysinger and A. Eisenberg, *Colloids Surf. B*, **1999**, *16*, 3-27.
6. R. M. Fuoss and U. P. Strauss, *J. of Polym. Sci.*, **1948**, *3*, 46-263.
7. R. F. Fedors, *Polymer*, **1979**, *20*, 225-228.
8. Y. Yang, *J. of Macromol. Sci.: Part B-Physics*, **2004**, *B43*, 845-858.
9. B. A. Wolf, *Macromol. Rapid Commun.*, **2007**, *28*, 164-170.
10. J. Eckelt, A. Knopf and B. A. Wolf, *Macromolecules*, **2008**, *41*, 912-918.
11. M. V. Badiger, N. R. Gupta, J. Eckelt and B. A. Wolf, *Macromol. Chem. and Phys.*, **2008**, *209*, 2087-2093.
12. F. Samadi, B. A. Wolf, Y. Guo, A. Zhang and A. Dieter Schluter, *Macromolecules*, **2008**, *41*, 8173-8180.
13. L. Ghimici, M. Nichifor and B. A. Wolf, *J. Phys. Chem. B*, **2009**, *113*, 8020-8025.
14. L. Ghimici, M. Nichifor, A. Eich and B. A. Wolf, *Carbohydrate Polym.*, **2012**, *87*, 405-410.
15. C.-E. Brunchi, M. Bercea, and S. Morariu, *e-Polymers*, **2009**, *065*, 1-10.
16. C.-E. Brunchi, M. Bercea and S. Morariu, *J. of Chem. & Eng. Data*, **2010**, *55*, 4399-4405.
17. C.-E. Brunchi, S. Morariu, M. Cazacu and M. Bercea, *Ind. & Eng. Chem. Res.*, **2010**, *49*, 12740-12746.
18. S. Morariu, C.-E. Brunchi, M. Cazacu and M. Bercea, *J. of Chem. & Eng. Data*, **2011**, *56*, 1468-1475.
19. R. Sartori, L. Sepulveda, F. Quina and F. Lissi, *Macromolecules*, **1990**, *23*, 3878-3881.
20. J. Rubio, *Colloids and Surfaces*, **1981**, *3*, 79-95.
21. E. Koksai, R. Ramachandran, P. Somasundaran and C. Maltesh, *Powder Technol.*, **1990**, *62*, 253-259.
22. J. Riley, "Charge in colloidal systems", in T. Cosgrove (Ed.) "Colloid science, principle, method and applications", Blackwell Publishing Ltd., Bristol, 2005, p. 14-35.