Libyan Journal of Basic Sciences (LJBS)
Vol: 16, No: 1 , P: 90- 100 , April. 2022 https://ljbs.omu.edu.ly/eISSN 2707-6261

Effect of changing the concentration of zinc oxide nanoparticles on the viscosity of the polyacrylamide / polyethylene glycol solutions

Najla Ali Elgheryani

Physics Department, Faculty of Education, University of Benghazi, Benghazi, Libya
Correspondence author: nagla.elgerani@uob.edu.ly

Abstract

In this work, Polyacrylamide/ Polyethylene glycol solutions of different molecular weights for Polyethylene glycol and different concentrations (17, 29, 38, 45 and 57 %) of ZnO nanoparticles were prepared by dissolving 0.5g of Polyethylene glycol in 20mL Polyacrylamide, then adding different concentrations of ZnO nanoparticles. Relative viscosity values are calculated by used the efflux time of the solutions, the viscosities(relative viscosity (η_r), specific viscosity (η_{sp}), reduced viscosity (η_{red}) and inherent viscosity (η_{int}) were calculated for all solutions, where measurements indicated an increase in these properties with increased concentration of ZnO nanoparticles and increased molecular weight of Polyethylene glycol. Viscosity is significant parameters during electrospinning process, and if the molecular weight increases, the viscosity of the solutions increase, making subsequent synthesis and purification more difficult. the constants K_H and K_K were calculated from the slopes of the viscosity values related to the Huggins and Kramer equations. These results can be used in many applications and scientific studies.

Keywords: polyethylene glycol, polyacrylamide, zinc oxide nanoparticles, viscosity, Huggins, Kramer.

Introduction

A polymer prepared by inverse emulsion polymerization has the advantages of rapid dissolution and narrow molecular weight distribution and avoids the defects of easy crosslinking and broad molecular weight distribution of products prepared by aqueous polymerization. Many excellent polymers have been prepared by inverse emulsion polymerization (*1*). The polymer flooding process uses polymers as viscosifying agents to improve the mobility ratio

and increase oil recovery (*2*). Polyacrylamide is a water-soluble synthetic polymer that possesses useful properties such as good adhesiveness, proper hygroscopicity, high hydrophilicity, and non-toxicity (*3*).

Polyethylene glycols below 700 molecular weight occur as clear to slightly hazy, colourless, slightly hygroscopic liquids with a slight characteristic odor. PEG's between 700-900 are semi-solid. PEG's over 1000 molecular weight are creamy-white waxy solids, flakes, or free-flowing powders. Water-soluble polyether polymers such as polyethylene oxide (PEO) and polyethylene glycol (PEG) are nontoxic, and biocompatible hence significantly participating in polymer blend technology(*4*). PEG is a versatile polyether being utilized in various applications, in particular in medicine (*5*) (PEO) is another name for (PEG) (*5*).

Zinc oxide is used in functional devices, catalysts, pigments, optical materials and many other important applications. ZnO nanopowders can be produced mechanochemically or solochemically (*6*). Nanoparticles, in general, possess enormous surface area per unit volume and have explicit characteristics. Zinc oside-based nanomaterials have been recognized to be of countless uses for numerous important requests from the beginning of nanoscience as a result of the great quantity of zinc element and the comparatively simple adaptation of its oxide to nanostructures (*7*). Polymer nanocomposites can be obtained by incorporating nanoscale inorganic materials into the host polymer (*8*)

Among the various inorganic nanometer materials, such as layered silicates, nanotubes, nanofibres, spherical nanoparticles like silica and nano-ZnO; sodium-montmorillonite as one of the natural layered silicates is very widely selected to make polymer-based nanocomposite owing to its intercalation/exfoliation characteristics, large specific surface, high aspect ratio, great ionic exchange capacity, low cost and good environmental benefit *(8).*Nanoparticles can be integrated with the polymer in several ways, it being worth to highlighting mixing with the polymer in an aqueous solution or inclusion by grafting or chemical functionalization on the nanoparticle surface (*2*).

A polymer's molecular weight is the sum of the atomic weights of individual atoms that comprise a molecule. It indicates the average length of the bulk resin's polymer chains. Not all polymer molecules of a particular

grade have the exact same molecular weight. There is a range or distribution of molecular weights. The average molecular weight can be determined by several methods (*9*). Viscosity is defined as the resistance of a liquid to flow (*10*), while viscoelasticity is defined as the ability of particular polymer solutions to behave as a solid and liquid simultaneously (*11*). This article investigates the effect of changing polyethylene glycol molecular weight on the viscosity of polyacrylamide/polyethylene glycol solution when concentrations of zinc oxide nanoparticles are changed.

Materials and Methods:

Materials:

In the present work, polyacrylamide solution (PAM: Mw (10000): 50% in H2O), zinc oxide nanoparticles (ZnO nanoparticles (100nm)) and Polyethylene glycol (PEG) with different molecular weights (8000, 10000 and 12000) used were supplied by Sigma-Aldrich GMBH.

Methods:

Four samples were used in this research; the first one is 20 mL of pure polyacrylamide solution, while the three other samples consist of 20 mL of polyacrylamide solution added to which 0.5 g of polyethylene glycol has a different molecular weights, then zinc oxide nanoparticles is added at a different concentration (17, 29, 38, 45 and 57%).

Measurements:

In determining the efflux time of the solutions, and methodology stated by ASTM was used. The efflux time for the first sample (20 mL of pure polyacrylamide solution) which was used as a solvent, and also the efflux time for the three other samples were measured by glass capillary viscometer.

The measured values have been expressed in terms of relative (η_r), specific (η_{sp}), reduced (η_{red}) and inherent (η_{int}) viscosities of all samples as follows (*12*, *13*):

$$\eta_r = \frac{t_{solution}}{t_{solvent}} \qquad (1)$$

$$\eta_{sp} = \eta_r - 1 \qquad (2)$$

$$\eta_{red} = \frac{\eta_{sp}}{C} = \frac{\eta_r - 1}{C} \qquad (3)$$

$$\eta_{inh} = \frac{Ln\,\eta_r}{C} \qquad (4)$$

Where C is the mass concentration of zinc oxide nanoparticles, $t_{solvent}$ is the efflux time of pure solvent and $t_{solution}$ is the efflux time of the samples. Then equations of Huggins (K_H) and Kramer (K_K) are defined as (*14, 15*):

$$\eta_{red} = [\eta]\,(1 + K_H\,.[\eta]\,.C \qquad (5)$$

$$\eta_{inh} = [\eta]\,(1 - K_K\,.[\eta]\,.C) \qquad (6)$$

[η] is the intrinsic viscosity where it is studied has been proposed as an effective method to assess polyacrylamide/polyethylene glycol affinity and the conformation of the polymers in solution (*16*).

Results and discussion:

The efflux time of polyacrylamide solution was measured at room temperature ($t_{solvent}$ = 245.45 sec), also the efflux time of the other samples was measured at room temperature (25^0 C), then relative viscosity values are calculated by equation1, for all polyacrylamide/polyethylene glycol solutions. The relationship between the relative viscosity values and the concentration of ZnO nanoparticles presented in Figure 1, it is noted from this figure, increasing relative viscosity of solutions with increasing the concentration of nanoparticles and increasing the molecular weight of polyethylene glycol (*17*).

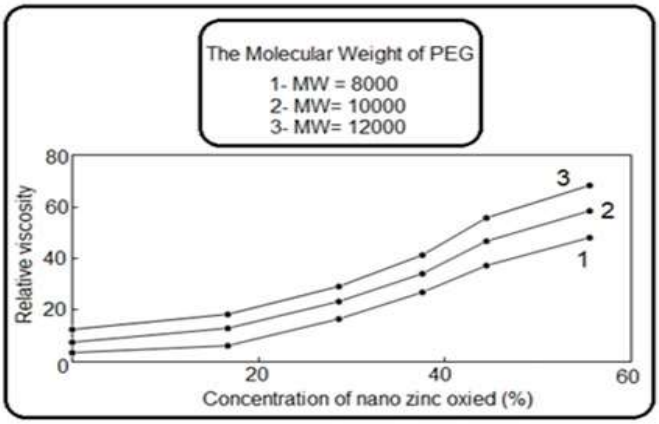

Figure 1: Relative viscosity vs. concentration of ZnO nanoparticles for PAM / PEG solutions 25°C.

The linear plots of Figure 2 show an agreement with Schulz-Blaschke equation for polyacrylamide / polyethylene glycol solutions. As shown in t Figure 2, the reduced viscosity and specific viscosity increases with increasing molecular weight of polyethylene glycol. Viscosity is significant parameters during the electrospinning process (*18*). When the viscosity is increased which means there will be a higher amount of polymer chains entanglement in the solution, the charges on the electrospinning jet will be able to fully stretch the solution with the solvent molecules distributed among the polymer chains (*19*). This is probably due to the greater resistance of the solution to be stretched by the charges on the jet (*19*).

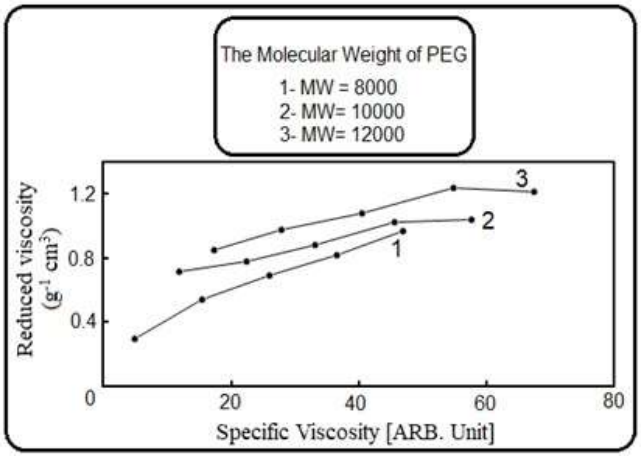

Figure 2: Reduced viscosity vs. specific viscosity for PAM / PEG solutions at 25° C.

Figure 3, the Huggins (K_H) and Kramer (K_K) plots are shown for PAM/PEG solutions (*16*). Huggins and Kramer coefficients are considered adequate criteria to evaluate the quality of the solvent(16) . The coefficients K_H and K_K can be calculated from the slopes of Figures 3, using equations 5 and 6 respectively. These constants depend on the solution state. The range for 0.25 to 0.5 in the Huggins coefficient (K_H) is assigned to good solvation (*20*). Moreover, negative values of K_K are attributed to good solvents (*20*).

As shown in Table 1 K_K has negative values at a molecular weight of 8000 for polyethylene glycol and the values of K_H ranged approximately from 0.41 to 0.45 at molecular weights of 10000 and 12000 for polyethylene glycol, these results indicate that polyacrylamide is a good solvent.

The Kraemer equation may not be valid for the whole range where the Huggins equation holds; one can see a slightly curved Kramer plot where the Huggins plot is linear. The Kramer plot is linear only at sufficiently low concentrations. Then, the following relationship holds between the dimensionless constants K_H and K_K

$$K_H + K_K = \frac{1}{2} \quad (7)$$

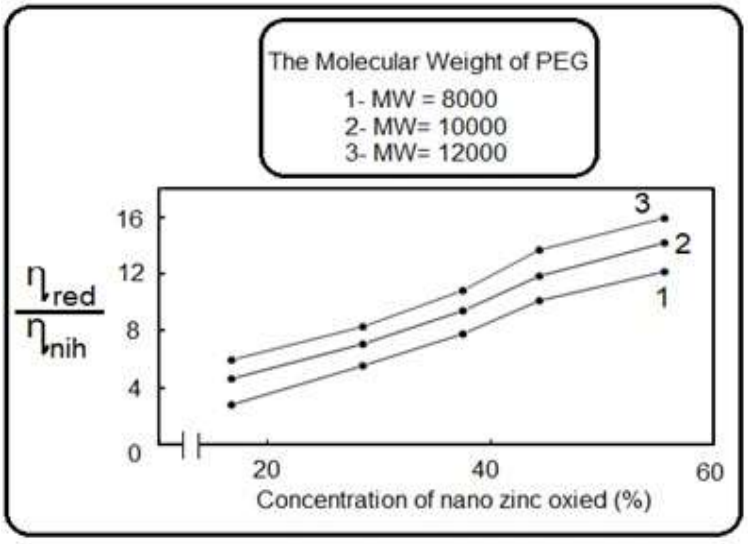

Figure 3: Huggins (K_H) and Kramer (K_k) plots for PAM / PEG solutions.

The results of this study indicate that the sum of K_H and K_K ranged from 0.4999 to 0.5004, as shown in tables 1 and 2.

Table 1: Huggins (K_H) and Kramer (K_k) for polyacrylamide/ polyethylene glycol solutions of 8000 and 10000 molecular weights for polyethylene glycol.

Concentration (%)	The molecular weight of PEG = 8000			The molecular weight of PEG =10000		
	K_H	K_k	$K_H + K_k$	K_H	K_k	$K_H + K_k$
17	0.75847	-0.25847	0.5000	0.40558	0.09443	0.50001
29	0.60391	- 0.10391	0.5000	0.42069	0.07930	0.4999
38	0.56872	- 0.06872	0.5000	0.42968	0.07032	0.5000
45	0.55235	- 0.05235	0.5000	0.43657	0.06344	0.50001
57	0.54264	- 0.04264	0.5000	0.44140	0.05860	0.5000

Table 2: Huggins (K_H) and Kramer (K_k) for polyacrylamide/ polyethylene glycol solutions of 12000 molecular weights for polyethylene glycol.

Concentration (%)	The molecular weight of PEG =12000			
	K_H	K_H	K_H	K_H
17	0.414789	0.414789	0.414789	0.414789
29	0.425867	0.425867	0.425867	0.425867
38	0.43441	0.43441	0.43441	0.43441
45	0.44043	0.44043	0.44043	0.44043
57	0.44449	0.44449	0.44449	0.44449

Logarithm reduced viscosity of the polyacrylamide/polyethylene glycol solutions represented in Figure 4 versus the concentration of ZnO nanoparticles in polyacrylamide/polyethylene glycol solutions, where the reduced viscosity increases with increasing concentration of ZnO nanoparticles. As shown in Figure 4, the relationship between Ln reduced viscosity and the concentration of ZnO nanoparticles has negative values at molecular weights 8000 and 10000 for polyethylene glycol, but has positive values at molecular weights 12000 for polyethylene glycol.

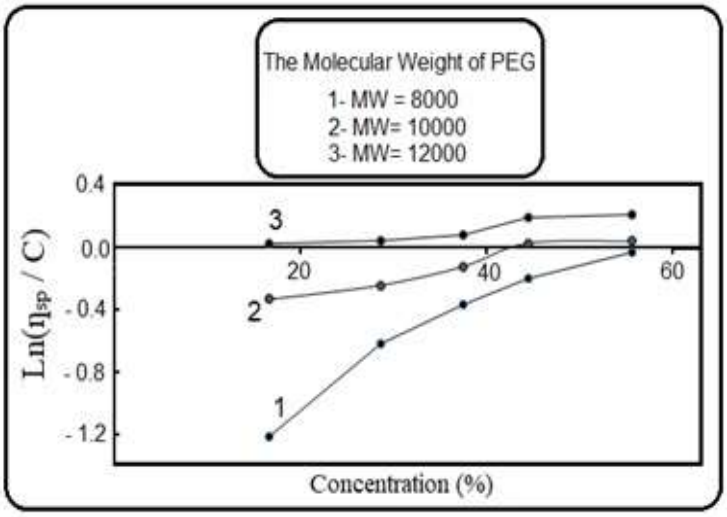

Figure 4: Ln Reduced viscosity vs concentration of ZnO nanoparticles for PAM / PEG solutions 25^{o}C.

Conclusion:

The figures of the viscosity of solutions indicate increased viscosity with increased concentration of ZnO nanoparticles and increased molecular weight of Polyethylene glycol. The treatment of viscosity data based on Huggins and Kraemer relationships allowed for evaluation of intrinsic viscosity of the polyacrylamide solutions with different molecular weight of Polyethylene glycol and different concentrations of ZnO nanoparticles. Viscosity is significant parameter during the electrospinning process. In this work, because, the molecular weight increases, the viscosities of the solutions increase, and that is making subsequent synthesis and purification more difficult. These properties can be used in medical, industrial applications and scientific studies.

References:

1. K. Yang, J. Chen, Q. Fu, X. Dun, C. Yao, Preparation of novel amphoteric polyacrylamide and its synergistic retention with cationic polymers. *e-Polymers* **20**, 162 (2020).
2. M.-C. Ruiz-Cañas, H.-I. Quintero-Perez, R.-H. Castro-Garcia, A. R. Romero-Bohorquez, Use of nanoparticles to improve thermochemical

resistance of synthetic polymer to enhanced oil recovery applications: a review. *CT&F-Ciencia, Tecnología y Futuro* **10**, 85 (2020).

3. M. I. Voronova, O. V. Surov, A. V. Afineevskii, A. G. Zakharov, Properties of polyacrylamide composites reinforced by cellulose nanocrystals. *Heliyon* **6**, e05529 (2020).
4. F. Zia *et al.*, in *Algae Based Polymers, Blends, and Composites*. (Elsevier, 2017), pp. 581-601.
5. P. Zarrintaj, M. R. Saeb, S. H. Jafari, M. Mozafari, in *Compatibilization of Polymer Blends*. (Elsevier, 2020), pp. 511-537.
6. M. Vaezi, S. Sadrnezhaad, Nanopowder synthesis of zinc oxide via solochemical processing. *Materials & Design* **28**, 515 (2007)
7. A. A Barzinjy, Structure, synthesis and applications of ZnO nanoparticles: A review. *Jordan Journal of Physics* **13**, 123 (2020).
8. C. Bai *et al.*, Preparation and properties of amphiphilic hydrophobically associative polymer/montmorillonite nanocomposites. *Royal Society open science* **7**, 200199 (2020).
9. S. Ebnesajjad. Effect of chemicals on plastics. (Elsevier, 2016), pp. xxvii-xli.
10. S. Ebnesajjad, *Concise Handbook of Fluorocarbon Gases: Applications in Refrigeration and Other Industries*. (John Wiley & Sons, 2021)
11. A. Rock, R. E. Hincapie, M. Tahir, N. Langanke, L. Ganzer, On the role of polymer viscoelasticity in enhanced oil recovery: extensive laboratory data and review. *Polymers* **12**, 2276 (2020)
12. S. P. Carvalho, E. F. Lucas, G. González, L. S. Spinelli, Determining Hildebrand solubility parameter by ultraviolet spectroscopy and microcalorimetry. *Journal of the Brazilian Chemical Society* **24**, 1998 (2013)
13. S. T. Shams-Abadi, S. M. A. Razavi, M. Irani, Intrinsic Viscosity and Molecular Parameters of Wheat Starch-Cress Seed Gum-Sucrose Mixture. *Biointerface Research in Applied Chemistry Platinum Open Access Journal.* , **11**, 12068 (2021)
14. N. O. Eddy, P. O. Ameh, C. E. Gimba, E. E. Ebenso, Rheological modeling and characterization of Ficus platyphylla gum exudates. *Journal of Chemistry* **2013**, (2013)
15. S. Taziki, S. M. A. Razavi, M. Irani, Intrinsic Viscosity and Molecular Parameters of Wheat Starch-Cess Seed Gum-Sucrose Mixture. *Biointerface Research in Applied Chemistry* **11**, 12068 (2021)
16. D. Marani, J. Hjelm, M. Wandel, Use of intrinsic viscosity for evaluation of polymer-solvent affinity. *Annual transactions of the nordic rheology society* **21**, 255 (2013)
17. W. Sun, G. Zhang, L. Pan, H. Li, A. Shi, Synthesis, characterization, and flocculation properties of branched cationic polyacrylamide. *International Journal of Polymer Science* **2013**, (2013)

18. Y. Zhao *et al.*, A facile method for electrospinning of Ag nanoparticles/poly (vinyl alcohol)/carboxymethyl-chitosan nanofibers. *Applied Surface Science* **258**, 8867 (2012).
19. H. Baheri, S. H. Bahram, Chitosan/nanosilver nanofiber composites with enhanced morphology and microbiological properties. *Journal of Textiles and Polymers* **3**, 64 (2015).
20. M. T. Acevedo, J. D. Laitano, M. F. Marrugo, A. P. Herrera, Á. Realpe, Intrinsic viscosity and chemical composition of the polyanhydridepoly (Sebacic acid-co-Azelaic acid) synthesized by microwave irradiation. *International Journal of Chemtech Research CODEN (USA)* **10**, 199 (2017).

تأثير تغيير تركيز جزيئات أكسيد الزنك النانوية على لزوجة جزيئات أكسيد الزنك في محاليل بولي أكريلاميد / بولي إيثيلين جلايكول

نجلاء علي الغرياني
قسم الفيزياء, كلية التربية, جامعة بنغازي

المستخلص العربي

في هذا العمل ، تم تحضير محلول بولي أكريلاميد / بولي إيثيلين جلايكول بأوزان جزيئية مختلفة للبولي إيثيلين جلايكول وتركيزات مختلفة (17 ، 29 ، 38 ، 45 ، 57٪) من جسيمات ZnO النانوية بإذابة 0.5 جم من البولي إيثيلين جلايكول في 20 مل بولي أكريلامي، تم إضافة تركيزات مختلفة من الجسيمات النانوية ZnO. حسب قيم اللزوجة النسبية من خلال وقت التدفق المستخدم للحلول ، وتم حساب اللزوجة (اللزوجة النسبية (η_r) ، واللزوجة المحددة (η_{sp}) ، واللزوجة المنخفضة (η_{red}) واللزوجة الكامنة (η_{int}) لجميع المحاليل ، حيث أشارت القياسات إلى زيادة في هذه الخصائص مع زيادة تركيز جزيئات ZnO النانوية وزيادة الوزن الجزيئي للبولي إيثيلين جلايكول. تعتبر اللزوجة معامل مهم أثناء عملية الغزل الكهربائي ، وإذا زاد الوزن الجزيئي ، تزداد لزوجة المحاليل ، مما يجعل التخليق والتنقية اللاحقة أكثر صعوبة. كما تم حساب الثوابت K_H و KK من منحدرات أرقام اللزوجة المتعلقة بمعادلات هاجينز و كرامي (Huggins , Kramer). يمكن استخدام هذه النتائج في التطبيقات الطبية والصناعية والدراسات العلمية

الكلمات المفتاحية : أكسيد الزنك النانوية ,الزوجة , جزيئات أكسيد الزنك ,بولي أكريلاميد / بولي إيثيلين جلايكول