Study the effect of Ag nanoparticles and ZnO nanoparticles at different concentrations on the viscosity and surface tension of Polyacrylamide solutions

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Abstract
Polyacrylamide Solutions of different concentrations (0.2, 0.4, 0.6, 0.8, 1.0 %) of Ag nanoparticles and ZnO nanoparticles were prepared, the viscosities and surface tension were measured for all solutions, where measurements indicated an increase in these properties with increased concentration, where the relative viscosity of polyacrylamide/zinc nanoparticles increased from 1.275 to 2.243, and the relative viscosity of polyacrylamide/silver nanoparticles increased from 1.178 to 1.934. Viscosity is significant parameters during electrospinning process. While the surface tension of the polyacrylamide/zinc nanoparticles has changed from 0.0343 Nm$^{-1}$ to 0.0527 Nm$^{-1}$, Also the constants $K_H$ and $K_K$ were calculated from the slopes of viscosity figures related to equations of Huggins and Kramer. These results can be used in medical, industrial applications and Scientific studies.

Key words
Constant of huggins, constant of kramer, relative viscosities ($\eta_p$), intrinsic viscosities [$\eta_i$], surface tension.

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Introduction
Polyacrylamide is a polymer formed from acrylamide subunits. It can be synthesized as a simple linear chain structure or cross-linked. It is highly water-absorbent, forming a soft gel when hydrated, used in such applications as polyacrylamide gel electrophoresis, and can also be called ghost crystals when cross-linked, and
in manufacturing soft contact lenses. In the straight-chain form, it is also used as a thickener and suspending agent. More recently, it has been used as a subdermal filler for aesthetic facial surgery.

Polyacrylamide (PAM), is an industrial organic polymer used in agricultural fields to stabilize the soil. In particular sandy placenta soils [1]. This material has proved many advantages such as low permeability and increase strength [1].

Silver (Ag) nanoparticles are widely used for their physical and chemical properties and are used in food, medical, industrial and other fields [2]. Silver nanoparticles are introduced into bactericidal agents. It is considered a means of transporting antibiotics [3]. Nanoparticles were used as colloidal silver, it has been studied extensively in the field of biotechnology, it is nontoxic and safe in the treatment of microbial diseases [4].

Structure of Zinc oxide (ZnO) nanoparticles, which has a small size, shapes and modified surface properties, led to the modification of the mechanical, optical and vibrational properties of the material [5]. Nanoparticles are sensitive to their surrounding air or solid molds where they affect the properties of mechanics and insulation [5]. Zinc nanoparticles have applications in the field of biomolecules, diagnostics and microelectronics[6]. Zinc nanoparticles can remove arsenic and sulfur from water, although bulk zinc oxide is unable to do so [6].

The Huggins equation is an empirical equation used to relate the reduced viscosity of a dilute polymer solution to the concentration of the polymer in solution [7].

The aim of present study is to improve some of polyacrylamide solutions properties (Viscosity and Surface tension) by nanoparticles technology, to be used in medical, scientific and industrial fields.

Experimental
1. Samples
   In the present work, polyacrylamide solution (PAM: Mw(10000): 50% in H₂O), Ag nanoparticles (100nm, 99.5% metal basis) and ZnO nanoparticles (100nm) used were supplied by Sigma-Aldrich GMBH.

   Solutions of different concentrations (0.2, 0.4, 0.6, 0.8, 1.0 %) of Ag nanoparticles and ZnO nanoparticles were prepared by dissolving in a 5 cm³ of nitric acid at room temperature, then mixed them with 40 cm³ of Polyacrylamide solutions.

2. Measurements
2.1 Viscosity measurements
   In determining the efflux time of the solutions, methodology stated by ASTM (1989) was used. The efflux time for solvents (nitric acid & pure solution polymer), polymers/silver nanoparticles solutions and polyacrylamide/zinc nanoparticles solutions were measured by glass capillary viscometer. The measured values have been expressed in terms of relative (ηr), specific(ηsp) and intrinsic ([η]) viscosities of all polyacrylamide/silver nanoparticles solutions and polyacrylamide/zinc nanoparticles solutions as follows [7-9]:

   \[ η_r = \frac{t_{solution}}{t_{solvent}} \quad (1) \]

   \[ η_{sp} = η_r - 1 \quad (2) \]

   \[ [η] = \frac{[2(η_{sp} - ln η_r)]^{1/2}}{C} \quad (3) \]

   where C is a concentration of the solution, t_{solvent} is the efflux time of pure solvent and t_{solution} is the efflux time of the polymer solution [10].
Then equations of Huggins (K_H), Kramer (K_K), and Martin (K_M) defined respectively as [8]:

\[ \eta_{sp} = [\eta] - K_H [\eta]^2 c \]  \hspace{1cm} (4)

\[ \frac{\ln \eta_r}{c} = [\eta] + K_K [\eta]^2 c \]  \hspace{1cm} (5)

\[ \frac{\ln \eta_{sp}}{c} = [\eta] + K_M [\eta] c \]  \hspace{1cm} (6)

2.2.2 Surface tension measurements

The drop-weight method, a counted number of drops were collected and the average mass of a drop found. The mean radius of the drop was determined, and then the surface tension (\( \gamma \)) against air expressed by the measured values as follows [10].

\[ \gamma = \frac{mg}{2\pi r} \]  \hspace{1cm} (7)

where \( m \) = average mass of a drop, \( g = 9.8 \text{ ms}^{-1} \), and \( r \) = internal radius of the tube used = 4mm. All measurements have been conducted at temperature 25 (± 0.1)\(^\circ\)C.

The surface tension force (F) and the surface tension energy (E) can be calculated by following equation, respectively [11].

\[ F = 4\pi r \gamma \]  \hspace{1cm} (8)

\[ E = \gamma A \]  \hspace{1cm} (9)

where A is a surfer area.

Results and discussion

1. The viscosity

The relative viscosity values of poly- acrylamide solutions with different concentrations of Ag nanoparticles and ZnO nanoparticles which are calculated by Eq.(1) against concentration of the two types of nanoparticles presented in Fig.1, it is note from this figure, increasing relative viscosity of solutions with increasing the concentration of nanoparticles, but the ZnO nanoparticles increased relative viscosity larger than the Ag nanoparticles. Viscosity is significant parameters during electrospinning process [12].

![Fig.1: Relative viscosity vs. different concentration of Ag nanoparticles and ZnO nanoparticles for polyacrylamide solutions at 25°C.](image)

As shown in Fig.2, the intrinsic viscosity decreased with increasing concentration of nanoparticles [13, 14]. However, the intrinsic viscosity which is calculated by Eq.(3) of polyacrylamide/ ZnO nanoparticles solutions still greater than that of polyacrylamide/Ag nanoparticles solutions.
Fig. 2: Intrinsic viscosity vs. different concentration of Ag nanoparticles and ZnO nanoparticles for polyacrylamide solutions at 25°C.

The specific viscosity ($\eta_{sp}$) of two types of solutions, which are calculated by Eq. (2), versus the concentration of Ag nanoparticles and ZnO nanoparticles for polyacrylamide solutions are plotted in Fig. 3, where it indicates an increase in the specific viscosity by increasing the concentration. The specific viscosity is dependent on concentration and interaction forces [7, 15].

Fig. 3: Specific viscosity vs. different concentration of Ag nanoparticles and ZnO nanoparticles for polyacrylamide solutions at 25°C.

Plots of $\frac{\eta_{sp}}{c}$ against the concentration, $\ln \frac{\eta_{sp}}{c}$ versus the concentration, $\ln \frac{\eta_{sp}}{c}$ against (ηsp), and $\frac{\eta_{sp}}{c}$ versus the concentration, as shown in Fig. 4-7 respectively, they are straight lines with the intrinsic viscosity as the intercept provided that the concentrations are not so high.

Fig. 4: Reduced viscosity vs. different concentration of Ag nanoparticles and ZnO nanoparticles for polyacrylamide solutions at 25°C.
The constants $K_H$ and $K_K$ can be calculated from the slopes of above figures, used Eq.(4) and (5) respectively. These constants depend on the solution state [15]. The range for 0.25 to 0.5 in the Huggins coefficient ($K_H$) is assigned to good solvation [8]. As shown in Table 1, values of $K_H$ ranged from 0.338 to 0.352 for solutions with different concentrations of Ag nanoparticles, but it ranged from 0.346 to 0.411 for solutions with different concentrations of ZnO nanoparticles.
Table 1: Huggins and Kraemer constants of solutions with different concentrations of Ag nanoparticles and ZnO nanoparticles.

| Concentration (%) | K_H of silver | K_K of silver | (K_H + K_K) of silver | K_H of ZnO | K_K of ZnO | (K_H + K_K) of ZnO |
|-------------------|---------------|---------------|-----------------------|------------|------------|---------------------|
| 0.2               | 0.337919      | 0.172081      | 0.5112                | 0.346271   | 0.153729   | 0.5150              |
| 0.4               | 0.341911      | 0.178089      | 0.5200                | 0.378423   | 0.153377   | 0.5318              |
| 0.6               | 0.345759      | 0.186341      | 0.5321                | 0.403264   | 0.139636   | 0.5429              |
| 0.8               | 0.349261      | 0.189739      | 0.5390                | 0.445216   | 0.120464   | 0.5657              |
| 1.0               | 0.351987      | 0.194813      | 0.5468                | 0.483281   | 0.092362   | 0.5756              |

For a Huggins solution, the Kraemer equation may not be valid for the whole range where the Huggins equation holds; one can see a slightly curved Kraemer plot where the Huggins plot is linear. The Kraemer plot is linear only at sufficiently low concentrations. Then, the following relationship holds between the dimensionless constants K_H and K_K [7].

\[ K_H + K_K = \frac{1}{2} \]  

(8)

The results of this study indicate that the sum of K_H and K_K is slightly greater than 0.5, as shown in Table 1.

3.2 The surface tension

Since the surface tension of the solutions increase with increasing concentration of silver nanoparticles as shown in Fig. 8, the surface tension force and surface tension energy increase as shown in Figs. 9 and 10 respectively. As a result, the forces of nanoparticles and the adjacent nanoparticles along with the forces of liquid molecules intervened in the liquid surfaces an attractive Van der Waals forces are exerted which increases the surface free energy and resulting the enhancement of surface tension [16].

![Fig.8: Surface tension vs. different concentration of Ag nanoparticles and ZnO nanoparticles for polyacrylamide solutions at 25°C](image-url)
**Fig.9:** Surface tension force vs. different concentration of Ag nanoparticles and ZnO nanoparticles for polyacrylamide solutions at 25°C.

**Fig.10:** Surface tension energy vs. different concentration of Ag nanoparticles and ZnO nanoparticles for polyacrylamide solutions at 25°C.

**Conclusions**

The figures of the viscosity of solutions indicate increased viscosity with increased concentration, but polyacrylamide/ ZnO nanoparticles solutions have viscosities higher than that of polyacrylamide/Ag nanoparticles. The treatment of viscosity data based on Huggins and Kraemers relationships allowed for evaluation of intrinsic viscosity of the polyacrylamide solutions with different concentration of Ag nanoparticles and ZnO nanoparticles. Viscosity is significant parameters during electrospinning process.

While the surface tension of polyacrylamide/Ag nanoparticles greater than surface tension of polyacrylamide/ ZnO nanoparticles solutions, as the surface tension increases by increasing the concentration. Van der Waals forces are exerted which increases the surface free energy and resulting the enhancement of surface tension. These properties can be used in medical, industrial applications and scientific studies.

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