Intermolecular Interactions Studies of ZnO-Tryptophan Suspension

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Abstract. The physicochemical properties (PCPs) have been studied to demonstrate the intermolecular interactions of ZnO nanoparticles (NPs) suspension. Tryptophan (Tryp) was dissolved in water and used as dilute solution to study the dispersion of ZnO NPs in different concentrations (25 to 150 µM) with 25 step. Density ρ, apparent molar volume V̂, refractive index (RI) nD and speed of light c have been reported. Man Singh equations were used to calculate the viscosity η, surface tension γ and friccohesity σ, activation energy ∆µ∗ was calculated using Arrhenius equation on the basis of pendant drop number (PDN) and viscous flow time (VFT) which counted by Borosil ManSingh Survismeter (BMS) instrument for solutions at room temperature. The physicochemical properties revealed the effect of ZnO NPs concentration on intermolecular interactions in dispersion systems. The results depicted the strong role of Tryptophan on ZnO NPs dispersion process in the term of solute–solvent and solute–solute interactions and free chemical reaction suspension.

1. Introduction

The nanoparticles have physicochemical properties differ from bulk materials and being emerged in many applications [1]. Nanoparticles suspension have attracted a lot of attention of researchers and manufacturers and designated as one of the nanotechnology approach to be more stable compared to micro particles suspension because of potent Brownian motion in nanofluids rather than micro fluids [2, 3]. Several physical methods are used to prepare nanoparticles suspension in one step or two steps including stirrers, ultrasonicators, magnetron sputtering system and high-pressure homogenizer [4]. The suspension of NPs has been recognized in different areas and applications such as biomedical, drug delivery, lubrications, magnetic fluids and heat transfer [5-11]. The agglomeration of NPs is actual challenge in nanofluids and many procedures were applied to maintain the stability of suspension to obtain homogeneous dispersion [12, 13] using additives such as surfactants or controlling pH value [14]. Dispersion of nanoparticles in water facilitated with polyethylene glycol showed good dispersion activity, and the optical density increased by increase the micro molar concentration of NPs [15, 16]. TiO2 [17, 18], Ag [19], chitosan [20], CeO2 [21] and Fe3O4 [22] NPs were used in dispersion processes to obtain homogeneous and stable suspension in different ways and promising outcomes were reported. The optical absorbance of ZnO NPs dispersed in aqueous tryptophan appeared in small peaks compared to absorbance of tryptophan in reverse way for first day.
dispersion, when the concentration of ZnO NPs increase, ZnO NPs absorbance increase and tryptophan absorbance decrease, unlike after seven days dispersion the absorbance of ZnO NPs disappeared [23]. Tryptophan is hydrophobic amino acid which being used in many fields including medical, diet, biosensor, anticancer, stress applications, reduction of fatigue, and antimicrobial activity [24-27]. The present work aimed to study the intermolecular interactions of dispersed ZnO NPs in aqueous Tryptophan media to assess the dispersion activity on the basis of physicochemical properties (PCPs) to demonstrate and enlighten the effect of ZnO NPs in suspension with the help of tryptophan. We chose ZnO NPs in this work due to their attractive properties among the metal oxide nanoparticles and found to be useful in potential applications such as biocompatible materials, anti-microorganism, cytotoxicity, ointments and creams. The results of this study may provide useful approach to explore dispersion activities of ZnO NPs with tryptophan and new path to enhance nanomaterials solubility and size reduction.

2. Experimental

2.1. Materials
Zinc oxide nanoparticles prepared elsewhere [23], tryptophan and water HPLC with spectroscopic grade (Molychem Company, India). All chemicals have been used without any further purification.

2.2. Preparation of suspension
Stock solutions of ZnO@Tryp-water (Ternary system) and Tryp-water (binary system) were prepared in micro molar concentration (150 µM) in 250 ml, respectively. Solutions were kept 30 minutes on stirrer followed by 30 minutes in ultrasonic bath (120 watt, 20 kHz, from Aczet). Further, the micro molar (µM) ZnO@Tryp-water solution was diluted using Tryp-water solution into six concentrations (25, 50, 75, 100, 125 and 150 µM). The solutions were kept in sealed volumetric flask avoiding contaminations and chemical reactions to be used for further studies after seven days. A schematic diagram of the experimental method implemented in this study is shown in Figure 1.

2.3. Physicochemical properties measurements
Density measurements were performed using a glass pycnometer (10 cm$^3$) with error ±10$^{-2}$ and weighted using analytical balance from Contech with accuracy 10$^{-3}$ gm. Refractive index (RI) was recorded by Abbe refractometer from BESTO with error ±10$^{-4}$. The PH variation of all samples was monitored using DBK ATC PH meter with error ±10$^{-2}$. Borosil Man Singh Surfismeter has been used to determine the viscosity, surface tension, friccohesity and activation energy by recording the pendant drop number (PDN) using digital counter and the viscous flow time (VFT) using racing watch (±0.01 sec) for all dispersion system concentrations. Data of both, binary and ternary systems are listed in Table 1. All measurements have been repeated three times at room temperature and the calibration was performed using distilled water.

3. Results and discussion

3.1. Apparent molar Volume ($V_\phi$)
Intermolecular interactions can be understood by studying the molar apparent volume, which indicates to the steady of the interaction by monitoring appearance of the molar volume after the process and its variation. It mainly depends on the density, which is in turn a good indicator of the solute-solvent and solute-solute interactions in dilute solutions. The density of suspensions increased by increase the micro molar concentration as shown in Table 1. The apparent molar volume $V_\phi$ (m$^3$·mol$^{-1}$) was calculated using densities data with the help of following equation (1):

$$V_\phi = \frac{1000 (\rho^0 - \rho)}{m \rho^0} + \frac{M}{\rho}$$  (1)
Where, $\rho^\circ$ and $\rho$ are the densities of the solvent and solution respectively, $m$ (10$^{-6}$ mol/L) is the molarity of solute and $M$ (kg·mol$^{-1}$) is the molar mass of solute [28]. The variation in apparent molar volume with an increase in micro molar concentration for both, DSF and DSW samples is reported in Figure 1.

Figure 1. Schematic diagram of the experiment

Figure 2. It is obvious from Figure 2 that $V_\phi$ decreases by increase the concentration which indicates that the interaction appears more effective by increase ZnO NPs concentration in dispersion system causing ion-ion interactions rather than ion-solvent interactions [29] keeping into account, the monitoring of pH value to assess the stability of dispersion to be maintained in normal value or small range variation [30, 31], in the all process the pH values were in normal range without any high or sudden change which indicates to stability of suspension for both dispersed samples as fresh prepared (DSF) and dispersed samples after one week (DSW), Table 1.

3.2. Speed of light

Speed of light in medium can be calculated on the basis of refractive index ($n_D$) which is defined as the ratio of the speed of light in a vacuum to speed of light in second medium. The speed of light, $C$ in suspensions was calculated with following equation:

$$C = \frac{3 \times 10^8}{n_D}$$  

(2)

The $3 \times 10^8$ ms$^{-1}$ is value of light speed in vacuum and $n_D$ is the refractive index. The variation in speed of light values with increase in micro molar concentration of ZnO NPs for both, DSF and DSW samples is plotted in Figure 3. It is observed from Figure 3 that, the values of speed of light vary and decrease by increasing ZnO NPs micro molar concentration which is theoretically reasonable with respect to the speed of light value in water and supported by behaviour of refractive index of dispersions.
Figure 2. Variation in Apparent molar volume with micro molar concentration of ZnO@Tryp-Water suspensions (a) fresh samples (DSF) (b) after 7 days (DSW) at room temperature.

Table 1: Density (ρ, ±10^{-3} g cm^{-3}), apparent molar volume, \(V_\phi\) (cm^3·mol^{-1}), refractive index (\(n_\rho\), ±10^{-5}), speed of light (C, ±10^{-3} m/s), pH (±10^{-2}), viscosity (η, mPa.s), surface tension (γ, mN m^{-1}), friccohesity (σ, s cm^{-1}) and activation energy (\(\Delta \mu_2^*\), kJmol^{-1}) for Tryp-Water and nanofluid (ZnO @ Tryp - Water) at (T= 298.15, ±1) for DSF and DSW.

| µM  | ρ   | \(V_\phi\) | \(n_\rho\) | Cx10^{8} | pH    | η     | γ     | σ     | \(\Delta \mu_2^*\) |
|-----|-----|-----------|----------|---------|-------|-------|-------|-------|------------------|
| 150 | 1.0343 | 197.207    | 1.3336   | 2.2496  | 8.15  | 1.0373 | 74.253 | 0.013970 | -72.687         |
| 25  | 1.0296 | 79.207     | 1.3334   | 2.2499  | 7.820 | 1.0286 | 74.451 | 0.013815 | -91.418         |
| 50  | 1.0336 | 78.738     | 1.3339   | 2.2490  | 7.790 | 1.0290 | 75.286 | 0.013667 | -91.634         |
| 75  | 1.0358 | 78.539     | 1.3342   | 2.2485  | 7.770 | 1.0299 | 76.001 | 0.013551 | -91.752         |
| 100 | 1.0376 | 78.391     | 1.3343   | 2.2484  | 7.750 | 1.0305 | 76.133 | 0.013536 | -91.840         |
| 125 | 1.0409 | 78.124     | 1.3345   | 2.2480  | 7.730 | 1.0308 | 76.375 | 0.013496 | -91.968         |
| 150 | 1.0425 | 78.002     | 1.3346   | 2.2479  | 7.760 | 1.0310 | 76.493 | 0.013478 | -92.030         |
|     |       |           |          |         |       |       |       |       |                  |
| 25  | 1.0295 | 79.219     | 1.3334   | 2.2499  | 6.960 | 1.0008 | 74.987 | 0.013346 | -90.530         |
| 50  | 1.0323 | 78.861     | 1.3336   | 2.2496  | 7.050 | 1.0017 | 75.744 | 0.013224 | -90.707         |
| 75  | 1.0341 | 78.689     | 1.3341   | 2.2487  | 7.120 | 1.0020 | 75.876 | 0.013205 | -90.792         |
| 100 | 1.0376 | 78.391     | 1.3344   | 2.2482  | 7.220 | 1.0026 | 76.133 | 0.013169 | -90.943         |
| 125 | 1.0393 | 78.256     | 1.3345   | 2.2480  | 7.330 | 1.0027 | 76.258 | 0.013148 | -91.004         |
| 150 | 1.0419 | 78.051     | 1.3345   | 2.2480  | 7.370 | 1.0035 | 76.449 | 0.013126 | -91.122         |
Figure 3. Variation in Speed of light with micro molar concentration of ZnO@Tryp-Water suspensions (a) (DSF) (b) (DSW) at room temperature.

3.3. Viscosity

Considering the flow and fluid motion, the internal friction forces have a noticeable effect in addition to the forces of adhesion with the wall of the vessel or tube. The more liquid molecules in the medium of the liquid, the less effect of the adhesion forces, and therefore, the flow is greater, unlike the particles which are close to the wall of the vessel or tube, the adhesive forces are added to the friction forces and limit the flow, taking into account the density of liquid and for this purpose the viscosity of the suspensions is studied, as it inevitably expresses the flow property of the fluids and explains this dynamical concept. VFT was used to calculate viscosity of suspensions using the following equation (3):

$$\eta = \left(\frac{\rho}{\rho_0}\right) \left(\frac{t}{t_0}\right) \eta_0$$  \hspace{1cm} (3)

Where $\rho_0$, $\rho$, $t_0$ and $t$ are the density and VFT of solvent and solution respectively, $\eta_0$ is a viscosity of media [32, 33]. The variation in viscosity with increase in micro molar concentration for DSF and DSW samples is reported in Figure 4 and Table 1. Figure 4 shows that the values of viscosity increase with increasing the micro molar concentration of ZnO NPs in the dispersion solutions for both, DSF and DSW. Generally, the viscosity of DSF is higher than viscosity of DSW, this may referred to the effect of Tryp that competes with ZnO NPs in the solutions and decreases the fluid mobility. The increment of the flow property causes increasing in friction forces of ZnO NPs @ Tryp-water suspension which promote the effect of hydrophilic - hydrophilic interactions where the Tryp induces the solute-solvent interactions making ZnO NPs interact effectively in the suspension and this may leads to decrease nano-size and affect the solubility, and that denotes to the strong effect of amino acid additive (Tryp) [23].
3.4. Surface Tension

The forces that affect the fluid molecules internally give a difference in the motion of the molecules whenever they go to the surface of the fluid. Since, the molecules in the depth of the liquid are surrounded by other molecules from all sides, this makes them in an almost uniform effect, but the matter is different at the surface of the fluid. The molecules dynamics become more restricted and repositioning in the solution to reduce the area and thus, appears tense and tight, this is known as surface tension, whether the liquid is in a container or in the form of drops due to the forces of cohesion. The surface tension of the dispersion system was calculated by the following equation (4) [32, 33]:

$$\gamma = \left( \frac{n_0}{n} \right) \left( \frac{\rho}{\rho_0} \right) \gamma_0$$ (4)

Where $n_0$ and $n$ are PDN of media and solution respectively, $\gamma_0$ is the surface tension of media. The variation in surface tension with increase in micro molar concentration for both DSF and DSW samples is represented in Figure 5 and Table 1. From Figure 5, it is clear that the values of surface tension increase with increasing the concentration of ZnO NPs in the suspension for both DSF and DSW. By increasing the concentration on ZnO NPs in the dispersion system, it is noticed that the solution surface becomes tenser and the solutions molecules cohere to each other at the surface. The presence of Tryp in ZnO NPs suspension leads to form tense drops due to increase the cohesive forces on the surface.

![Figure 4. Variation in viscosity with micro molar concentration of ZnO@Tryp-Water suspensions (a) (DSF) (b) (DSW) at room temperature.](image-url)
3.5. Friccohesity

If the effect of the friction and cohesion forces in liquids is combined and interconnected to be measurable and assessable, a new and wonderful concept will be deduced, which is friccohesity. Friccohesity is already introduced by Man Singh and has become used in fluid dynamics and physiochemical properties studies. The friccohesity of dispersion systems has been calculated using Man Singh equation (5):

$$\sigma = \frac{\eta_0}{\gamma_0} \left( \frac{t}{t_0} \right) \left( \frac{n}{n_0} \right)$$ \hspace{1cm} (5)

Where $\eta_0$ and $\gamma_0$ are reference viscosity and surface tension respectively, $t_0$ and $t$ are the VFT of media and solution respectively, $n_0$ and $n$ are PDN of media and solution respectively [32,33]. The variation in friccohesity with increase in micro molar concentration for both DSF and DSW is plotted in Figure 6. From Figure 6 it is observed that, the friccohesity of ZnO NPs suspension in the presence Tryptophan, decreased with increasing concentration of ZnO NPs due to product of intermolecular forces effect. The more release of $\text{Zn}^{2+}$ and dipoles of water induced ion-dipole interaction by increasing ZnO NPs concentration and leads to weaker interconnected forces which can be explained by the friccohesity behaviour, Table 1.

3.6. Activation Energy

In molecular interaction, an amount of energy which stimulates the reaction to take place should be taken into account to keep the interaction free from any chemical change. This energy must be small and not reach the limit that allows a chemical reaction to establish. The interaction must be in the mode of solvent, solute, dipoles, ions interactions and intermolecular collisions. They study of activation energy concept for dispersion systems is the important factor, otherwise, the interaction will jump to new chemical stage which disturbs the intermolecular interaction and hence the dispersion activity will be interrupted. The activation energy ($\Delta \mu_2^*$, j/mol) was calculated with following equation (6) :

$$\Delta \mu_2^* = RT \left\{ \ln \left( \frac{\eta_0 V_1}{hN} \right) - \left[ \frac{1}{V_2} \left( 1000\eta - (V_1 - V_2) \right) \right] \right\}$$ \hspace{1cm} (6)
Where $R$ is gas constant, $T$ is solution temperature (room temperature), $h$ is Planck constant and $N$ is Avogadro number, $V_1$ is the solute volume and $V_2$ is the solvent volume [32, 33]. The variation in activation energy with increase in micro molar concentration for both DSF and DSW samples is reported in Figure 7. It is obvious from Figure 7 that the activation energy decreases in negative direction for all samples which promote molecules orientations because at lower activation energy greater proportion of the collision between solute-solvent including more molecules in the collisions and it is observed that the activation energy for DSW is higher than DSF in general, which revealed the strong effect of Tryp and may cause the dissolving of ZnO NPs if the suspension kept for a time more than one week, this gives a glance to use Tryptophan to increase solubility of ZnO NPs in such applications that prefer soluble NPs rather than dispersion [23].

![Figure 6](image1)

**Figure 6.** Variation in Friccohesity with micro molar concentration of ZnO@Tryp-Water suspensions (a) (DSF) (b) (DSW) at room temperature.

![Figure 7](image2)

**Figure 7.** Variation in Activation energy with micro molar concentration of ZnO@Tryp-Water suspensions (a) (DSF) (b) (DSW) at room temperature.
4. Conclusion
In this study, the intermolecular interactions of ZnO@Tryp-water suspension have been studied on the basis of physicochemical properties such as density $\rho$, apparent molar volume $V^\phi$, refractive index $n_D$, speed of light $C$, viscosity $\eta$, surface tension $\gamma$ and friccohesity $\sigma$, and activation energy. The reported properties used to demonstrate the dispersion activity of ZnO NPs and the results revealed the effect of micro molar concentration of ZnO NPs on the dispersion process and variation was observed with strong role of tryptophan appeared obviously in the outcomes, which induce the interaction toward decreasing the particle size or to be soluble in water rather than dispersion. This might be beneficial in many applications that use ZnO NPs as a solute like ointments, sunscreen, skin creams, microorganism swimmers fighting and biological studies.

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