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Experimental static light scattering study on the scattering parameters for Pluronic

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Abstract

Static light scattering from an aqueous solution of Pluronic F-108 prill has been measured over the angles range (40^o to 140^o) for four different concentrations (0.004, 0.006, 0,008, 0.01 gm/ml). A home build multiangle static light scattering experiment was used to calculate the Rayleigh ratio R_θ and construct the Zimm plot, which was used to calculate the radius of gyration$\langle \boldsymbol{R_G} \rangle$, the second virial coefficient A_2, and the molecular weight M_W. The refractive index was measured by abbe's refractometer to calculate refractive index increment $(\mathrm{dn/dc})$. The measured data show that the molecular weight of Pluronic F-108 prill is 14661 gm/mole, which is a medium molecular weight. The second viral coefficient is greater than zero, which means that the Pluronic F-108 prill likes the solvent (deionized water) more than itself. While the radius of gyration $\langle \boldsymbol{R_G} \rangle$ is 1094 nm, which is a little bit large as in an aqueous environment these block copolymers self-assemble into micelles.

Keywords: Laser scattering, static laser scattering, pluronic

1. Introduction

Pluronic (Poloxamer) is one of the important biomedical polymers that is arranged in an A-B-A triblock structure, which gives PEO-PPO-PEO block copolymer fig. (1), the polyethylene oxide part (PEO) is hydrophilic while the polypropylene oxide part (PPO) is hydrophobic [1]. In an aqueous environment and above the critical micelles concentration[2], these block copolymers self-assemble into micelles. Poloxamer is effectively used in the pharmaceutical field as solubilizers, emulsifiers, absorption enhancers, solid dispersion carriers, and stabilizers drugs [3,4].

Light scattering is the redirection of light that takes place when light interacts with matter. There are two types of scattering, elastic scattering (the wavelength of the scattered light is the same as the incident light) and inelastic scattering (the scattered radiation has a wavelength different from that of the incident radiation) [5]. The scattered light intensity and wavelength can be used to get precious information about the scattering material. The evaluation of the intensity fluctuations with time is commonly named dynamic light scattering (DLS) [6], while the analysis of the mean intensity is known as static light scattering (SLS). Which gives information about the average molecular weight M_w of the macromolecule, the radius of gyration $\langle \boldsymbol{R_G} \rangle$ and the second virial coefficient A_2[7].

The scattered light intensity was measured at the angles range (40^o to 140^o) for the different concentrations (0.004 to 0.01 gm/ml) of the solution by the static light scattering experiment. The angular distribution of scattered light intensity is used by the Debye equation to measure the scattering parameters of the used polymer (Pluronic F-108 prill) [8-10]. The refractive index was measured using abbe refractometer to get the refractive index increment since Debye equation shows the importance of measuring the refractive index increment [11].

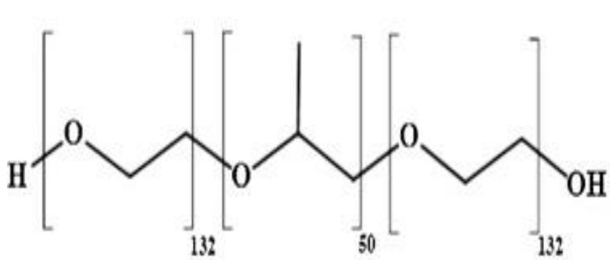

Fig. (1) Chemical structure of Pluronic F-108 prill.

2. Experimental details

Pluronic F-108 prill was dissolved in deionized water at room temperature to make a stock solution of concentration 0.01 gm/ml. this stock was diluted to make solutions of concentrations $c_1 = 0.004$, $c_2 = 0.006$, $c_3 = 0.008$, $c_4 = 0.01$ gm/ml. Abbe's refractometer was used to measure the refractive index n for the different concentrations c of the solution.

The scattered light intensity I_θ was measured at the angles range (40° to 140°) for the different concentrations of the Pluronic F-108 prill solution by the static light scattering experiment as shown in fig. (2). The dilute solution of the Pluronic F-108 prill was kept in a cuvette with a monochromatic laser source of wavelength 650 nm passed through it. The intensity of the scattered light from the solution was recorded by a photomultiplier tube at an angle θ with respect to the direction of the incident laser.

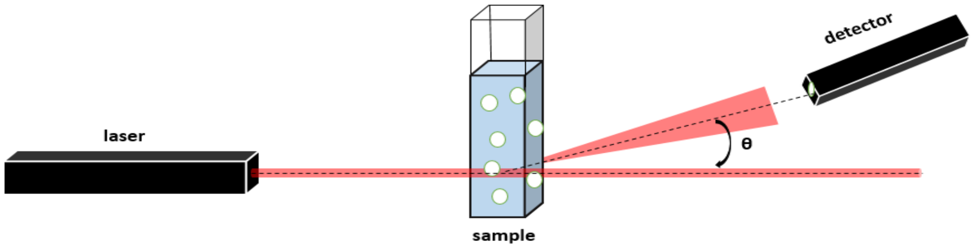

Fig. (2) Experimental setup of static light scattering.

3. Results and discussion

The refractive index was represented against the concentration of the prepared solutions in Fig. (3), the intercept with the ordinate represents the refractive index of the solvent n_0 eq. (1). Fig. (4) shows the representation of $\frac{\Delta n}{\Delta c}$ against the concentration (c), the intercept with the ordinate represents the refractive index increment $\frac{dn}{dc}$.

$$n = n_o + \left(\frac{dn}{dc}\right) c \qquad (1)$$

Fig. (5) shows the angular distribution for Pluronic F-108 prill with different concentrations.

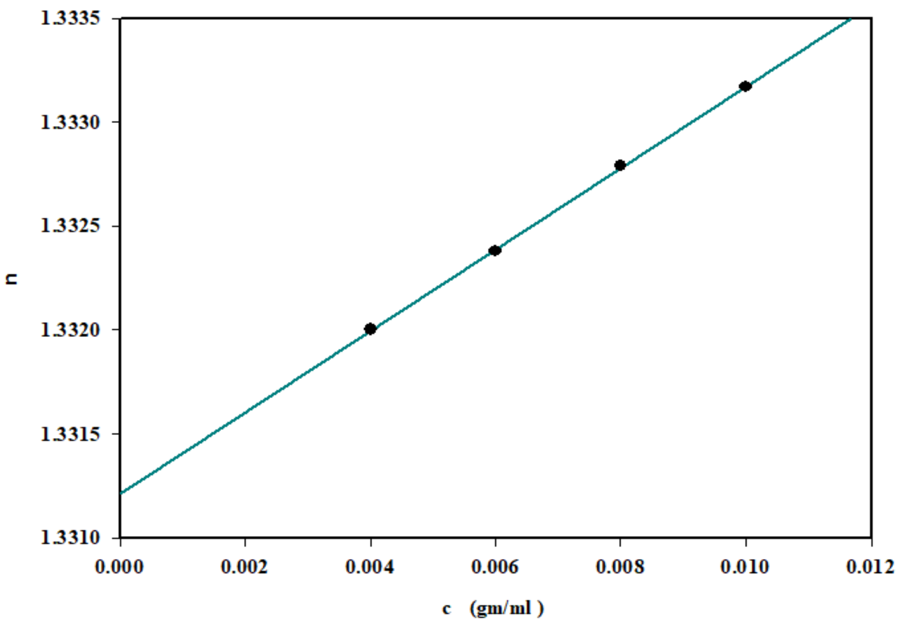

Fig. (3) Relation between the refractive index (n) and concentration (c) of Pluronic F-108 prill dissolved in deionized water.

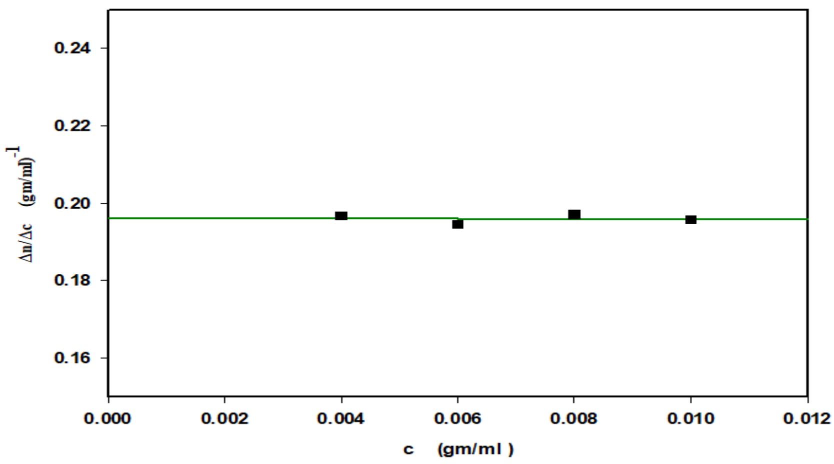

Fig. (4) Relation between ($\frac{\Delta n}{\Delta c}$) and concentration (c) of Pluronic F-108 prill dissolved in deionized water.

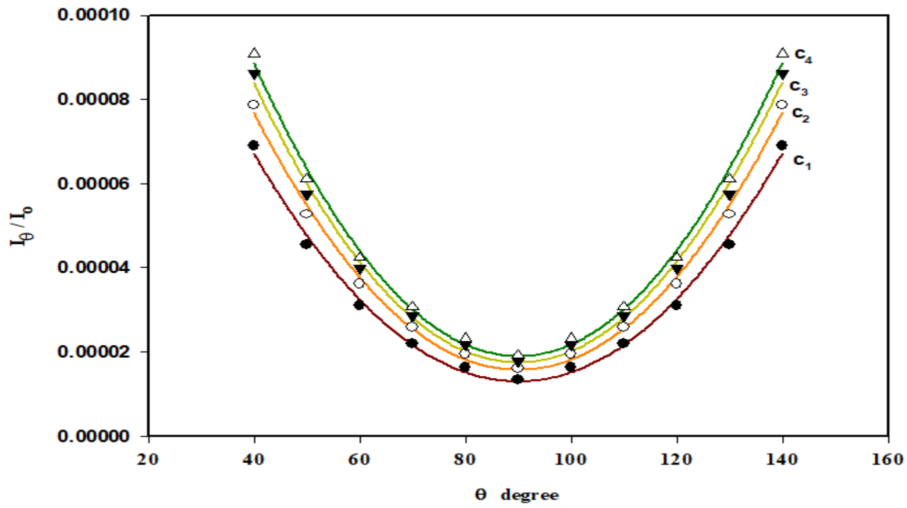

Fig. (5) Angular distribution for Pluronic F-108 prill dissolved in deionized water at different concentrations.

The scattering from the Pluronic F-108 prill solution can be described by the following equations [12-13]

$$\frac{Kc}{R_\theta} = \frac{1}{M_W}\left[1 + \frac{16\,\pi^2}{3\,\lambda^2}\langle {R_G}^2\rangle \sin^2\left(\frac{\theta}{2}\right)\right] + 2A_2 c \quad (2)$$

$$K = \frac{2\pi^2 {n_0}^2}{N_A \lambda^4}\left(\frac{dn}{dc}\right)^2 (1+\cos^2\theta) \quad (3)$$

$$R_\theta = \frac{I_\theta\, r^2}{I_0\, V} \quad (4)$$

K is the optical constant, $\boldsymbol{N_A}$ is the Avogadro's number, $\boldsymbol{\lambda}$ is the wavelength of light, $\boldsymbol{V}$ the scattering volume, $\boldsymbol{I_0}$ is the incident light intensity, $\boldsymbol{r}$ is the distance between the scattering volume and the detector, and $\boldsymbol{R_\theta}$ is the Rayleigh ratio which eliminates the influence of the experimental conditions such as the scattering volume, the distance r…. etc.

The values of $\frac{Kc}{R_\theta}$ were calculated using equations (2) to (4), the $\frac{Kc}{R_\theta}$ values were represented against the concentration c for angles ranging from 40° to 90° as shown in fig. (6). The intercepts with the ordinate represent the values of $\frac{Kc}{R_\theta}$ at $c = 0$ for the different angles.

The $\frac{Kc}{R_\theta}$ at $c = 0$ were represented against $\sin^2\left(\frac{\theta}{2}\right)$ as shown in fig. (7). The $\langle \boldsymbol{R_G}^2\rangle$ can be calculated from the slope and the $\boldsymbol{M_W}$ from the intercept, since eq. (2) was reduced to eq. (٥) as $c = 0$ [14-18].

$$\frac{Kc}{R_\theta} = \frac{1}{M_W}\left[1 + \left(\frac{16\pi^2}{3\lambda^2}\right)\langle {R_G}^2\rangle \sin^2\left(\frac{\theta}{2}\right)\right] \quad (٥)$$

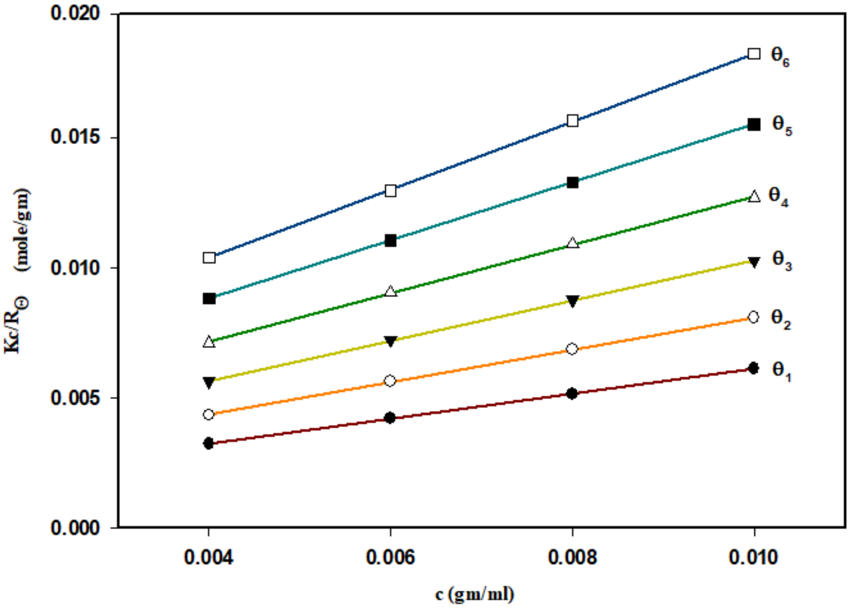

Fig. (6) $\frac{Kc}{R_\theta}$ of different angles ($\theta_1 = 40°, \theta_2 = 50°, \theta_3 = 60°, \ldots \ldots \ldots, \theta_6 = 90°$) vs concentration (c) for Pluronic F-108 prill dissolved in deionized water.

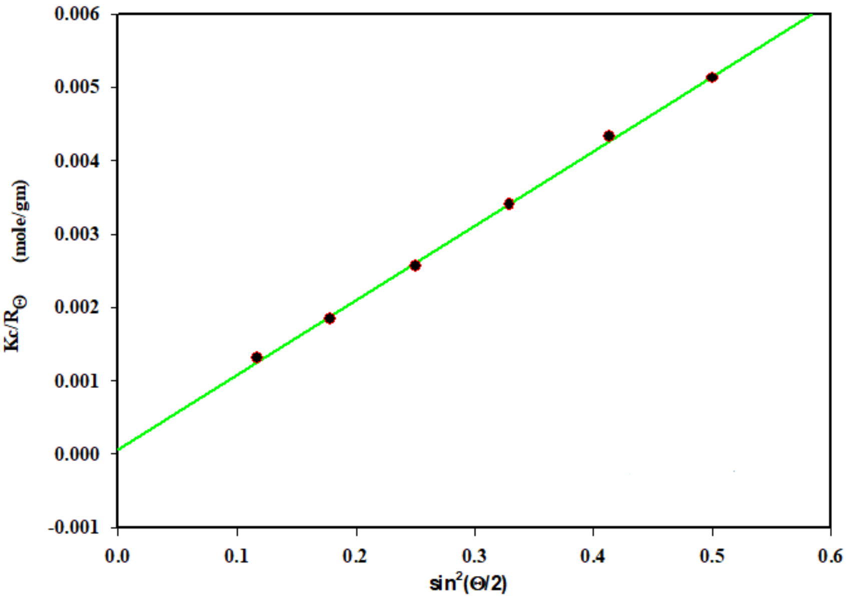

Fig. (7) $\frac{Kc}{R_\theta}$ vs Sin^2(θ/2) at c=0 for Pluronic F-108 prill dissolved in deionized water.

Similarly, fig. (8) shows the measured values of $\frac{Kc}{R_\theta}$ vs $\sin^2\left(\frac{\theta}{2}\right)$ for different concentrations $c_1 = 0.004$, $c_2 = 0.006$, $c_3 = 0.008$, $c_4 = 0.01$ gm/ml. The values of $\frac{Kc}{R_\theta}$ for the different concentrations at $\theta = 0$ were calculated from the intercepts with the ordinate. These calculated values were represented against the concentration c in fig. (9). The A_2 can be calculated from the slope and the M_W from the intercept, since eq. (2) was reduced to eq. (6) as $\theta = 0$[14-18].

$$\frac{Kc}{R_\theta} = \frac{1}{M_W} + 2A_2c \qquad (٦)$$

The second viral coefficient has one of the following values [19]

1. $A_2 > 0$, the solute likes the solvent's molecules more than its' molecules (good solvent for the given solute).
2. $A_2 < 0$, the solute likes its' molecules more than the solvent's molecules (bad solvent for the given solute, the solute may aggregate).
3. $A_2 = 0$, the solute-solvent strength is equivalent to the solute-solute interaction strength (an ideal solvent)

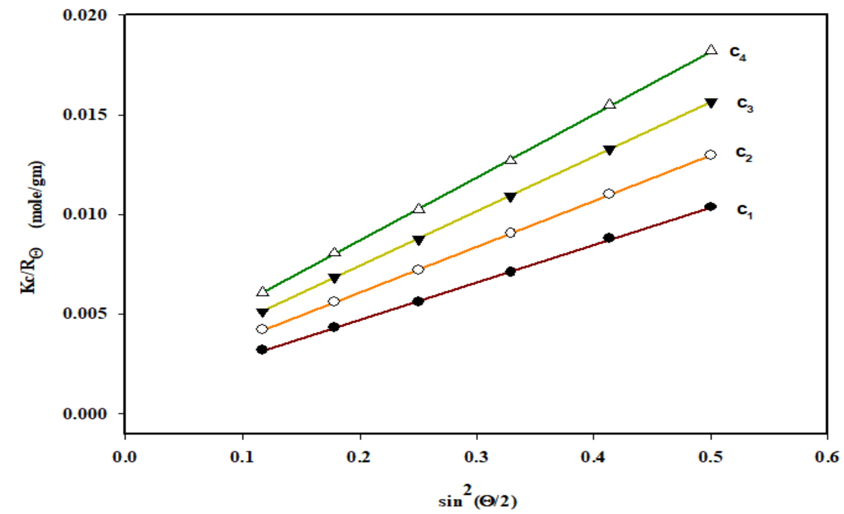

Fig. (8) $\frac{Kc}{R_\theta}$ of different cncentrations vs $\sin^2(\theta/2)$ for Pluronic F-108 dissolved in deionized water.

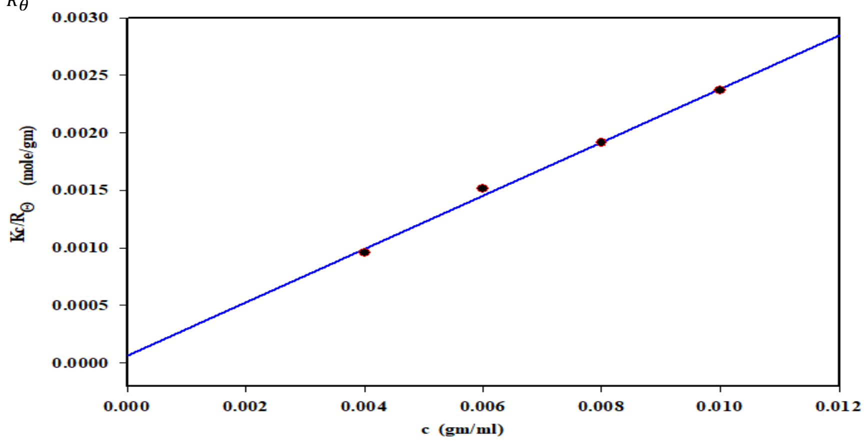

Fig. (9) $\frac{Kc}{R_\theta}$ vs concentration (c) at $\sin^2(\theta/2) = 0$ for Pluronic F-108 prill dissolved in deionized water.

Zimm plot Construction

Zimm plot was constructed by combining fig. (6) to fig. (9) in the same plot by plotting $\frac{Kc}{R_\theta}$ vs $\sin^2(\theta/2) + kC$ (k take value that makes the concentration term comparable to the $\sin^2(\theta/2)$ term) get a grid as shown in fig.(10) [20-22].

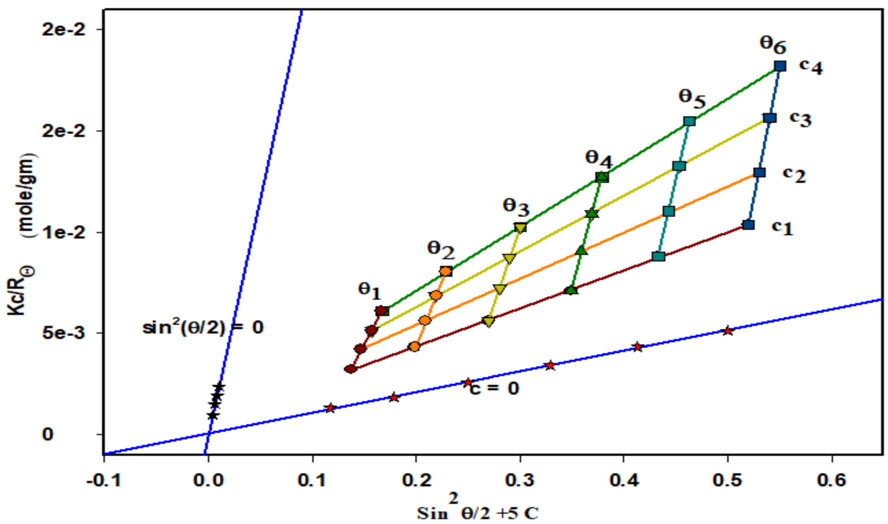

Fig. (10) The Zimm plot for Pluronic F-108 prill dissolved in deionized water.

Table (1) The scattering parameters of Pluronic F-108 prill dissolved in deionized water.

Molecular weight M_w	14661 gm/mole
The second viral coefficient A_2	0.1158 mole.ml.gm^{-2}
The radius of gyration $\langle R_G \rangle$	1094 nm
Refractive index increment $\frac{dn}{dc}$	0.1962 *ml/gm*
Refractive index of the solvent	1.3312

5. Conclusion

Pluronic F-108 prill was dissolved in deionized water to make four solutions with different concentrations (0.004, 0.006, 0.008, 0.01 gm/ml). Using abbe's refractometer to measure the refractive index and then calculate the refractive index increment.

The scattered light scattering intensity was measured by the home build multiangle static light scattering experiment for all angles (40^o to 140^o) and different concentrations. This data was used to construct the Zimm plot. The measured data table(1) shows that the molecular weight of Pluronic F-108 prill was 14661 gm/mole, which is a medium molecular weight. The second viral coefficient was greater than zero which means that the Pluronic F-108 prill likes the solvent (deionized water) more than itself (good solvent for the Pluronic F-108 prill). While the radius of gyration $\langle R_G \rangle$ was 1094 nm, which is a little bit large as in an aqueous environment these block copolymers self-assemble into micelles.

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