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Full Length Article

Determination of scattering parameters of polyvinyl alcohol by static laser scattering

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ABSTRACT

Static laser scattering (SLS) is one of the most efficient techniques used for the molecular weight determination of polymer. Among of all polymers, polyvinyl alcohol (PVA) polymer was selected. A polystyrene (PS) was used as a standard polymer. A polyvinyl alcohol was investigated for its importance in pharmaceutical, biomedical, and industrial applications. Different concentrations in the range (3–9) × 10^{-3} g mL^{-1} were prepared. SLS data were obtained by using a self-built of the laser scattering system. The angular behavior of those selected polymer solutions with different concentrations were studied by plotting the intensity of the scattered light against the scattering angle in the range of 40–140°. By using Zimm plot the weight-average molecular weight $\mathbf{M_w}$, radius of gyration $\mathbf{R_G}$, and second virial coefficient $\mathbf{A_2}$ of the standard PS and PVA were determined.

1. Introduction

A polyvinyl alcohol is a popular polymer its density 1.26 g/ml at 25 °C and its glass transition temperature 85 °C. This polymer is used as relief of symptoms of dry eye and artificial tears, paper, Wood Processing, and Building Industry. The chemical formula of polyvinyl alcohol is shown in (Fig. 1).

Scattering method is one of the most accurate techniques for the determination of polymer's molecular weight. Measuring scattering from large solute molecules with a relatively small wavelength. The strength of this technique; it is a quite sensitive, has a wide range of molecular weight determination, typically from about 10^4 to 5×10^6 g mol^{-1}, absolute method that does not need calibration, and can give the radius of gyration and the second virial coefficient (Li, 2008; Stevens, 1998).

The different concentrations of the polymer solution give different refractive indices. As a result of the fluctuation in refractive index; the incident light will be scattered by each illuminated macromolecule in all directions.

The basic parameters yielded by light scattering measurements of a dilute polymer solution are the weight-average molecular weight, radius of gyration, and second virial coefficient, for large molecules.

The phenomenon of the light scattering from dilute polymer solution is based on rigorous theory, which is a combination of physical optics and thermodynamics (Brown, 1996).

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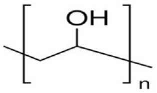

Fig. 1 – Chemical formula of polyvinyl alcohol polymer.

The theory is rather complex, as testified by the fact that it was developed by no lesser personages than Einstein and Debye. In the theory of light scattering the concept of small and large particles is important.

Small particles are meant particles or macromolecules, which are much smaller than the wavelength of incident light. Such particles behave as a point source of scattered light. In experimental practice, particles smaller than (λ/20) of light can be treated as small particles, and particles larger than (λ/20) of light called large particles (Ghazy, 2011).

Therefore, the scattering of visible light is one of the fundamental experimental techniques of the physical chemistry of polymers. In the mood of what is called, the classical or static laser scattering (SLS), which is known as Rayleigh scattering.

In the present work we had built a laser scattering system by which we had measured the angular distribution of the scattered laser light. From these data we had determined the weight-average molecular weight $\mathbf{M_w}$, radius of gyration $\mathbf{R_G}$, and second virial coefficient $\mathbf{A_2}$. The selected polymers are polyvinyl alcohol and, our system standard by polystyrene.

Light scattering in case of small particles, the average Molecular weight of polymer can be determined from its contribution to the overall intensity of light scattered from its dilute solution. This contribution equals the difference between the scattered intensities of the solution and pure solvent. In order to eliminate the influence of specific experimental conditions, such as intensity of the incident beam, its polarization, the geometry of the apparatus, a quantity for the normalized scattered light intensity, called the Rayleigh Ratio of symbol (R_θ) has been defined. The subscript (θ) denotes the angle at which the scattering intensity has been measured. At infinite dilution, the intensity of light scattered from a solution of uniform small macromolecules is described by the simple Equation (Sun, 2004):

$$\frac{kc}{R_\theta} = \frac{1}{M_W} \tag{1}$$

where c is the concentration of the solute, M_w is the weight-average molecular weight, and k is the optical constant (Sperling, 2006) and is defined as:

$$k = \frac{2\pi^2 n_o^2 \left(\frac{dn}{dc}\right)^2}{\lambda^4 N_A}\left(1+\cos^2\theta\right) \tag{2}$$

where:

n_o: the refractive index of the solvent,
λ: the wavelength of the incident light in vacuum,
N_A: Avogadro's number; and
dn/dc: the specific refractive index increment.

The value of k depends on the polymer, solvent, and temperature. For highly dilute solutions, the differential ratio can be replaced with no loss of accuracy by the ratio (Δn/c), which is a quantity easy to measure, where Δn is the difference between the refractive indices of the solution and solvent.

With molecular solutions, the colloidal particles consist of small gel particles, i.e., the coiled chain molecules which have become solvated with solvent to extent that the entire gel particles consist of 90–99 % of solvent. In this case, the refractive index of the solution differs slightly from the solvent's refractive index. This gives rise to simple physical laws for the scattering of light (Siddiq et al., 1997; Siddiq and Wu, 1997).

The basic equation which describes the light scattering from dilute solutions of no uniform small macromolecules according to P. Debye is usually written as:

$$\frac{kc}{R_\theta} = \frac{1}{M_W} + 2A_2c + \left(3A_3c^3 + \cdots\right) \tag{3}$$

where A_2 and A_3 are the second and third virial coefficients respectively (Sun, 2004) and:

$$R_\theta = \frac{I_\theta r^2}{I_0 V} \tag{4}$$

where:

I_θ: the scattered intensity,
I_o: the incident intensity,
r: the distance between the sample and detector; and
V: the scattering volume.

The second virial coefficient is an important thermodynamic characteristic of the polymer-solvent system. High values of A_2 are characteristic of system with intense interaction between the polymer and solvent, that means of a good solvent for the given polymer.

To determine the molecular weight of a polymer which has molecules smaller than λ/20 (where λ is the wavelength), we measure the intensity of light scattered from two to four solutions with different concentrations, calculate the ratio kc/R_θ, most frequently kc/R_{90} and plot them as a function of polymer concentration. The intercept with the axis of ordinatesmgives the reciprocal value of M_w according to Eq. (1) (Shere et al., 1996) and the slope of the concentration dependence being twice the value of A_2.

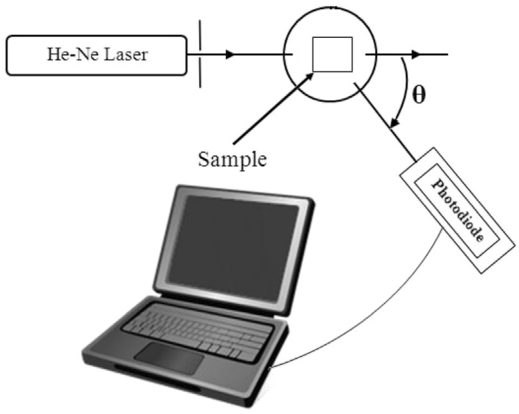

Fig. 2 – Schematic diagram of static laser scattering (SLS) measurement experiment set-up.

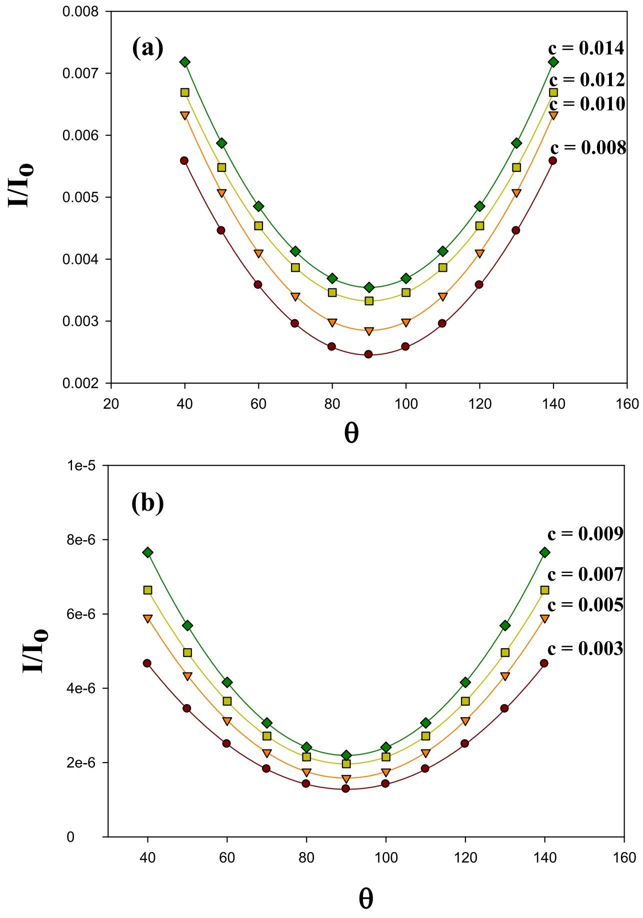

Fig. 3 – (a) The angular distribution of light scattering measurements for PS dissolved in DMF at different concentrations, (b) The angular distribution of light scattering measurements for PVA dissolved in water at different concentrations.

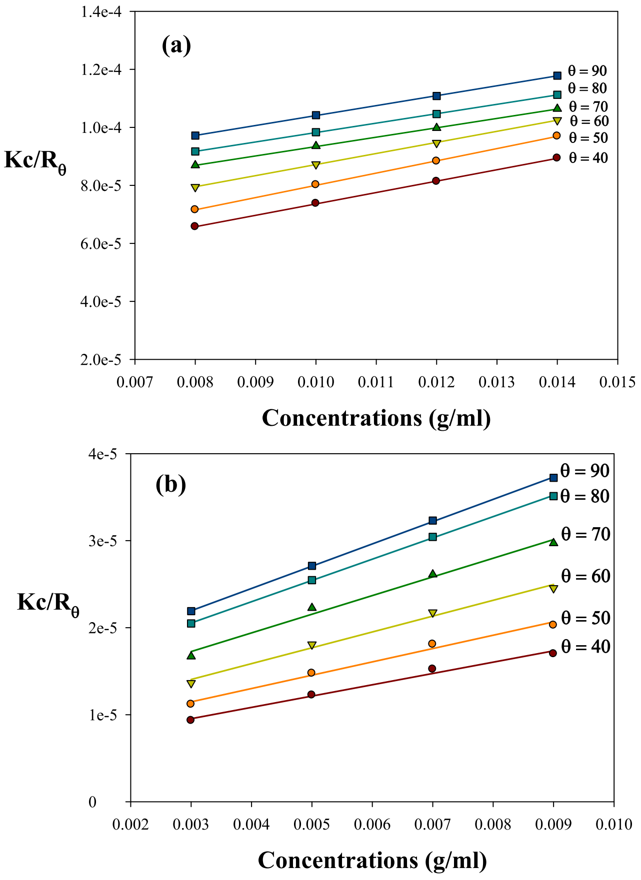

Fig. 4 – (a) kc/R$_\theta$ of Polystyrene dissolved in DMF, as a function of the concentration c at constant angle, (b) Kc/R$_\theta$ of PS dissolved in water, as a function of the concentration c at constant angle.

In this simple way, i.e., through the measurement of scattered light intensity at a single angle θ, the molecular weight can be obtained but only for particle diameters smaller than $\lambda/20$, which is only found in a number of proteins and polymers. For such polymer, any observation angle can be selected from the scattering function is symmetrical. However, for experimental reasons, it is usually selected at 90° (Wu et al., 1996).

However, in case various mass points of a large particle reaches the detector with different phase and interferes giving rise to the phenomenon of intraparticle or intramolecular interference, which results in a decrease in the intensity of scattered light. There is just one direction at which no interference occurs no matter what the size of the particle is, this is the direction of the incident beam, i.e., at an angle of observation zero (Ghazy, 2011).

Unfortunately, at this angle no measurement can be made, because the weak scattered beam is virtually lost in the primary beam, of intensity larger by many orders of magnitude. For practically all polymer molecules occurring in common experimental practice, the extent of interference increases with increasing angle of observation. Unlike for small particles, for large particles the intensity of scattered light depends on the angle of observation. The angular dependence of the scattered intensity is pre-determined by the size and shape of the scattering particles.

Thus, at least on principle, it must be possible to obtain some information on the size and shape of the scattering particles from the angular dependence of scattering intensity (Ghazy et al., 1999).

The basic equation describing light scattering from dilute solutions of non-uniform large macromolecules at finite concentrations is usually written in the form:

$$\frac{kc}{R_\theta} = \frac{1}{M_W}\left[1 + \frac{16\pi^2}{3\lambda^2}\langle R_G^2\rangle \sin^2\left(\frac{\theta}{2}\right) + \cdots\right] + 2A_2c + 3A_3c^3 + \cdots \quad (5)$$

where, $<R_G^2>$ is the square of the average radius of gyration and the angle brackets indicate that the value has to be averaged over all possible conformation and the other symbols defined above.

Equation (5) tells that, in order to determine the weight-average molecular weight, the average radius of gyration, and the second virial coefficient of a polymer solute in a given solvent, angular dependence of the scattering intensity have to be measured for several (usually four) solutions with different concentrations. Then, the values of the ratio (Kc/R$_\theta$) are calculated for all experimental points and two sets of dependence are constructed, the angular dependence of (Kc/

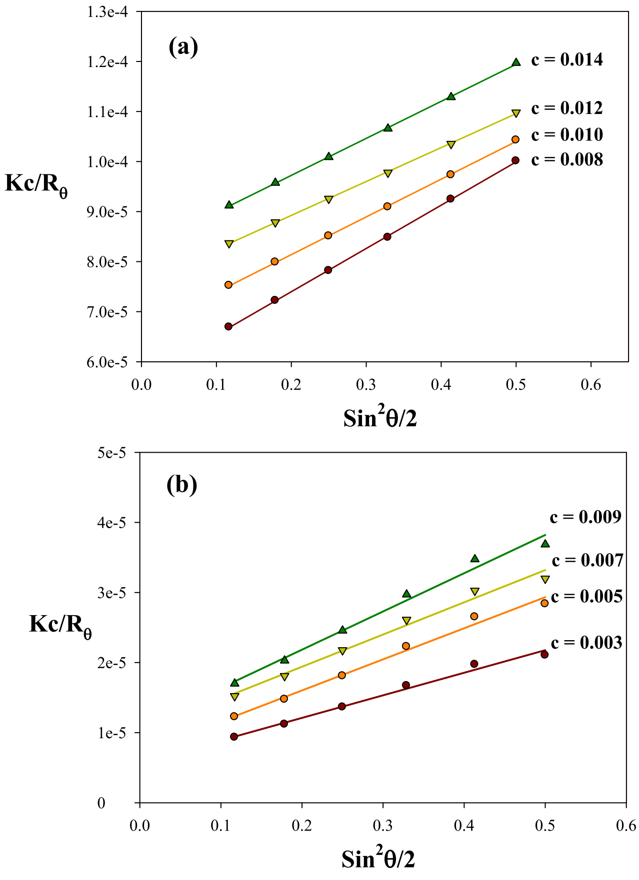

Fig. 5 – (a) Kc/R$_\theta$ of PS dissolved in DMF, as a function of the observation angle at constant concentration, (b) Kc/R$_\theta$ of PVA dissolved in water, as a function of the observation angle at constant concentration.

R$_\theta$) at constant concentrations and the concentration dependence of (kc/R$_\theta$) at the individual angles of measurement.

The angular dependence is extrapolated to zero angle of measurement to eliminate the intramolecular interference and the concentration dependence is extrapolated to infinite dilution, i.e., to zero concentration, to eliminate the intramolecular interference. Through the extrapolated points, two extrapolated dependence are plotted, via the extrapolated angular dependence for infinite dilution and the extrapolated concentration dependence for zero angle of measurement, both extrapolations are conveniently made graphically in one diagram called the Zimm plot. The two extrapolations provide the most needed information.

The ordinate of the common intercept of the two extrapolations with the y-axis is the reciprocal value of the weight-average molecular weight of the investigated polymer. The initial slope of the extrapolated angular dependence for infinite dilution is proportional to the average radius of gyration and the initial slope of the concentration dependence for zero angle of measurement is proportional to the second virial coefficient (Frato, 2003).

In general, it can be taken as a rule: For polymers with small chain macromolecules with molar masses smaller than (2×10^5), a standard light scattering measurement yields the weight-average molecular weight and the second virial coefficient (Ghazy, 2011).

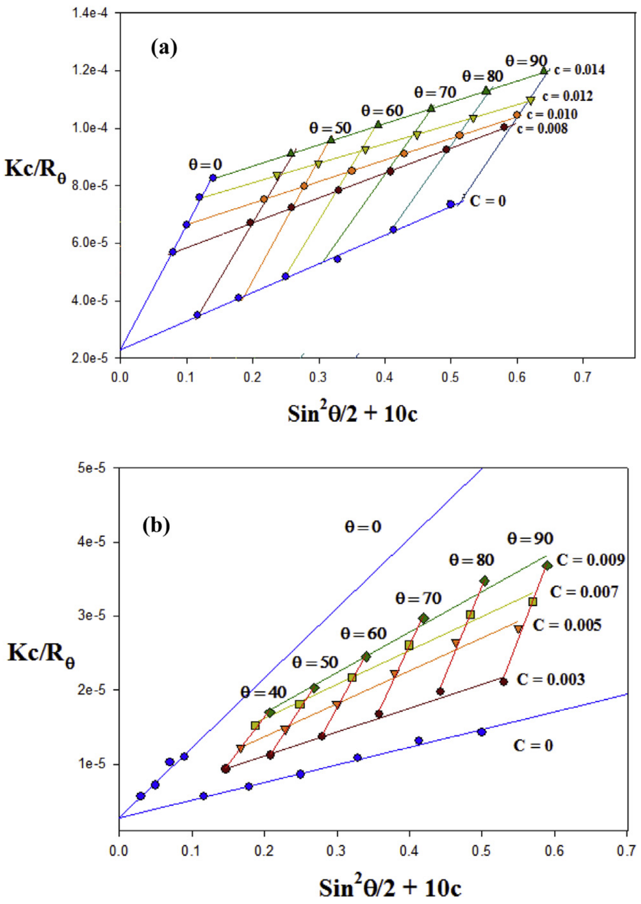

Fig. 6 – (a) Zimm plot of Polystyrene dissolved in DMF, (b) Zimm plot of polyvinyl alcohol dissolved in water.

For present laser light scattering measurements, the chain molecules of the polymers that we used are of diameters larger than (λ/20). Therefore, the weight-average molecular weight must be determined by measuring the scattered light intensity as a function of the scattering angle.

The Zimm treatment (Ghazy, 2011) affords the most accurate graphical procedure for the derivation of light scattering parameters when angular dependence comes into play. It is seen from Eq. (5) that the factor (kc/R$_\theta$) has a linear dependence on the concentration c (for constant angle of observation) and a linear dependence on $\sin^2(\theta/2)$.

The first step in the construction of Zimm plot is to carry out angular distribution of light scattering measurement at different constant concentrations from 40 to 140°. The results obtained are plotted graphically as (kc/R$_\theta$) versus c at constant angle θ and (kc/R$_\theta$) versus $\sin^2(\theta/2)$ at constant concentration c.

That graphical representation yields a series of straight lines which can be extrapolated to the ordinate and therefore, permit determination of (kc/R$_\theta$) at $c \to 0$ and (kc/R$_\theta$) at $\theta \to 0$.

Therefore, in Eq. (5), at $c \to 0$, we can get the form:

$$\frac{kc}{R_\theta} = \frac{1}{M_W}\left[1 + \frac{16\pi^2}{3\lambda^2}\langle R_G^2\rangle_z \sin^2\left(\frac{\theta}{2}\right)\right] \tag{6}$$

Also at $\theta \to 0$, the equation will be in the form:

$$\frac{kc}{R_\theta} = \frac{1}{M_W} + 2A_2c \tag{7}$$

Table 1 – Results for polystyrene dissolved in DMF and polyvinyl alcohol dissolved in water.

Polymer	M_W (g mol^{-1})	A_2(mol ml g^{-2})	R_G (nm)
Polystyrene	43478 (El-Baradie et al., 2000)	2.17×10^{-3}	109
Polyvinyl alcohol	353356(Liu et al., 1999)	4.71×10^{-4}	162

According to the above equations, the values of (kc/R_θ) as a function of the concentration c at a constant angle of observation θ and (kc/R_θ) as a function of the angle θ at constant concentration c is obtained. Then, they are represented in a new graph (Zimm graph) as straight lines.

In the same single diagram, one plot (kc/R_θ) versus $\sin^2(\theta/2) + Kc$. where K is an arbitrary number; to make the concentration term comparable with $\sin^2(\theta/2)$ and extrapolate the resulting lines at constant concentration and a constant angle to give a grid. The extrapolated points at different angles for zero concentrations (according to Eq. (6)) are extrapolated to zero angle, i.e., to cut the Kc/R_θ axis and similarly the points of zero angle at different concentration (according to Eq. (7)) are extrapolated to zero concentration. Ideally, the two extrapolations should cut the (kc/R_θ) axis at the same point. The reciprocal of the intercept, $[kc/R]_{c=0}^{\theta=0}$ is equal to the weight average molecular weight of the polymer.

The initial gradient of the graph at zero angles gives a measure of the second virial coefficient A_2. Thus, $A_2 = 1/2$ (initial slope of $\theta = 0$ line. From line $c = 0$ we can get the radius of gyration (Li et al., 1997; Wu, 1997).

2. Materials and method

2.1. Chemicals

Dimethylformamide (DMF HPLC grade, Fisher), polystyrene was purchased from Sigma–Aldrich (Cat. No. 33165-1) and polyvinyl alcohol was purchased from Oxford Laboratory Reagent (Cat. No. 9002-89-5).

2.2. System set-up

In this work we use a Meredith 2 mW, 543 nm Green He–Ne laser, rotator stage, and Pasco Xplorer GLX photodiode connected to computer as shown if (Fig. 2).

2.3. Sample preparation

Sample preparation must be in a clean bottle and it's very important to avoid any contaminations (particles, greases, and surfactants) all interacts with polymer, or bubbles in the mixture.

PS is dissolved in DMF, and PVA is dissolved in distilled water at boiling. Scattering measurements were performed for the concentrations 0.008, 0.010, 0.012, 0.014 g/ml of PS, and concentrations 0.003, 0.005, 0.007, and 0.009 g/ml of PVA.

3. Result and discussion

Fig. 3 represents the angular distribution of the scattering intensities of PS dissolved in DMF and. Also PVA dissolved in distilled water.

The result of (kc/R_θ) as a function of the concentration for a selected at constant observation angle; corresponding to those (θ) values we obtain straight lines. Also, a plot of (kc/R_θ) at a constant concentration as a function of $\sin^2(\theta/2)$ is constructed and also yield straight lines. In both plots the straight lines are extrapolated to the (kc/R_θ) axis to get the values of zero lines. As shown in (Fig. 4 and 5), respectively.

Zimm plot for PS dissolved in DMF and PVA dissolved in water is plotted by using 4 concentrations and 6 scattering angles. This makes a grid of 24 data The extrapolation values for $(kc/R_\theta)_{c=0}$ versus the $\sin^2(\theta/2)$ (at $c = 0$) values are plotted. Also the extrapolated values from $(kc/R_\theta)_{\theta=0}$ are plotted versus the concentration c, (at $\sin^2(\theta/2) = 0$). To obtain two straight lines represent the zero lines. The intercept of these two lines with the yields ($1/M_w$). From the slope of line $\sin^2(\theta/2) = 0$ we can obtain the value of A_2 where the slope is equal to $2A_2$. Zimm plots are shown in (Fig. 6). Table 1 shows all obtained parameters.

4. Conclusion

We have constructed an experiment for measuring the angular distribution of light scattered intensity of scattering angles from (40–140°). The angular distribution of scattered intensity of polystyrene dissolved in DMF as a standard polymer and polyvinyl alcohol dissolved in water at four different concentrations. By using this data in a Zimm plot we calculated the weight-average molecular weight of two polymers in agreement with the stammered values. Also important parameters are calculated using the same Zimm plot those are radius of gyration of each polymer, also the second virial coefficient for the solvent for each polymer is determined. This proves that one can use this experiment to determine the precise value of the molecular weight for unknown polymers.

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