

## Dissymmetries and Radii of Gyration of Cellulose Acetate by Light Scattering Techniques

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**Summary :** A wide range of concentration ( $1.0 \times 10^{-4}$  to  $6.0 \times 10^{-2}$  g/ml) of cellulose acetate in acetone is considered and dissymetry of all these concentrations is measured at different angles from  $45^\circ$  to  $90^\circ$  at intervals of  $5^\circ$  degree. These dissymmetries are measured by using two wave lengths (436 nm. and 546 nm.) of incident light. An equation is derived for the dependence of dissymetry upon angle of measurement, considering the system as coil-like molecules. Making use of this equation and Zimm plot method, the radii of gyration of these solutions are measured. It is concluded that one gets the same results by both the methods. It is further concluded that the radius of gyration increases as the concentration decreases.

### Introduction

The properties of the polymer are dependent upon size, molecular weight and their distribution. Therefore it is necessary to know these parameters before their use. For the determination of these parameters, especially size distribution, light scattering is the best method, being an absolute, and applicable to a wide range of concentration. Due to extensive production and utility of cellulose acetate polymer, we have considered this polymer for investigation.

Little work has been done upon this polymer and especially by light scattering. In 1946 Stein<sup>1</sup> et al. considered four fractions of this polymer in acetone. They found molecular weight, size of the polymer, by using dissymetry<sup>2,3,4</sup> and turbidity<sup>5,6</sup> method. They concluded that the shape of the polymer changes with the change in molecular weight. Subramanian<sup>7</sup> et al. tried to find out the exact size of the polymer, by dissymetry method. They dyed the sample to different extents, by using different dyes for this purpose. They obtained even larger values than without dying. They suggested that this may be due to the extension in the polymer as a result of dying. To overcome this problem and the problem of interference, we have studied a wide range of concentration. In this way the dependence of molecular weight and second virial coefficient of the polymer upon concentration were studied. These parameters were determined by using

turbidity<sup>6</sup> method and these are given some where else<sup>8</sup>

In this work the radii of gyration of cellulose acetate polymer are determined by using dependence of dissymetry upon angle of measurement<sup>9</sup>. The values determined in this way are compared with each other and the results obtained for the same parameter in the same system by a well established Zimm plot method<sup>10,11</sup>

### Theoretical

There are mainly two light scattering methods, which are used for determination of size or radius of gyration, i) Zimm plot method<sup>10,11</sup>, which is a double extrapolation method and needs refractive index of solvent and refractive index increment of the system. This method gives  $z$ , the average radius of gyration of the polymer. Furthermore being laborious, the exact values of concentration of the system and many instrumental constants are also required. The following equation is used, in this method.

$$\left( \frac{Kc}{R_\theta} \right)_{\substack{c=0 \\ \theta=0}} = 1/MP + 2Bc$$

or

$$\left( \frac{Kc}{R_\theta} \right)_{\theta=0} = \frac{1}{M} \left( 1 + \frac{16\pi^2}{3\lambda^2} R_g^2 \sin^2 \theta / 2 \right) + (1) + 2BC + \dots \quad (1)$$

here K is an optical constant and is given as

$$K = 2\pi^2 n_0^2 \left( \frac{dn/dc} \right)^2 / N \lambda^4 \quad (2)$$

$n_0$  is the refractive index of the solvents  $dn/dc$  is the refractive index increment of the system,  $\lambda$  and  $M$  are the wave length of the incident light and molecular weight of the polymer respectively.  $R_g$ ,  $B$ , and  $R_\theta$  are the radius of gyration, second virial coefficient and Rayleigh<sup>12</sup> ratio respectively.  $P_\theta$  which is known as particle scattering function, and becomes equal to one as  $\theta$  approaches to zero, is related to Rayleigh ratio<sup>13</sup> as

$$P_\theta = R_\theta / R_0, \text{ where } R_\theta \text{ and } R_0$$

are the Rayleigh ratios determined for theta and zero degree angles respectively. ii) The dissymetry<sup>2,3,4</sup> method, which is defined as the ratio of the scattered intensities measured at two angles symmetrical to 90° (usually 45°/135° is considered) and gives an approximate size of the polymer. This approximate size is determined by using either the diagrams<sup>2</sup> or the tables<sup>14,15</sup> giving the relation of dissymetry to  $D/\lambda$ , where  $D$  is the major length of the polymer. The mathematical representation of dissymetry is as<sup>2,3,4</sup>

$$Z = \frac{I_{45^\circ} / I_{135^\circ}}{I_{45^\circ} / I_{135^\circ}} = \frac{P_{45^\circ} / P_{135^\circ}}{R_{45^\circ} / R_{135^\circ}} \quad (3)$$

$$Z_\theta = I_\theta / I(180-\theta) = P_\theta / P(180-\theta) = R_\theta / R(180-\theta) \quad (4)$$

In these equations all the symbols have the same meaning as before. For making use of the diagrams or the tables for the determination of size, some assumptions are required. Firstly the system should be monodisperse or the degree of polydispersity should be known and secondly the shape of the polymer should be known or supposed.

The literature<sup>1-4,7, 14-19</sup> survey shows that though the method gives approximate and doubtful results, however it is used for the size determination of the

polymers. In (1978) young<sup>9</sup> et al. introduced a new method, by which (without any supposition about polydispersity and double extrapolation) radius of gyration of the system can be found. They used it to find the radius of gyration of the micelles. They concluded that the micelles were rod-like molecules. We will derive a similar equation for coil-like molecules, and apply it for the determination of their radius of gyration. The  $P_\theta$  values for coil-like molecules is given as<sup>20</sup>

$$P_\theta = 2/w^2 (e^{-w} + w + 1) \quad (5)$$

$$\text{where } w = \mu^2 R_g^2 \text{ and } \mu = (4\pi/\lambda) \sin \theta / 2.$$

The equation (5) is for flexible and monodisperse system only. For polydisperse system the value of  $P_\theta$  is given as<sup>21</sup>

$$P_\theta = 2/u (uN_n - 1) N_w N_n u \quad (6)$$

$u = \mu^2 b^2 / 6$  and  $b$  is the statistical length of the monomer,  $\mu = 4\pi/\lambda \sin \theta / 2$ .  $N_n$  and  $N_w$  are the number average and weight average degree of polymerization respectively. For stiff and polydisperse system, similar equation was given by Peterlin<sup>22</sup>

Considering the dissymetry ratio<sup>2,3,4</sup> in term of  $P_\theta$ , and  $P_\theta$  value as given by Debye<sup>20</sup>

$$Z = P(\theta) / P(180-\theta) \quad (7)$$

$$Z = 2/w^2 (e^{-w} + w - 1) / [2/w^2 (e^{-w} + w + 1)] \quad (8)$$

$$\text{here } W = \frac{4\pi}{\lambda'} \sin^2 \frac{\theta}{2}$$

$$\text{and } W' = \frac{4\pi}{\lambda'} R_g^2 \sin^2 (180-\theta)/2$$

On simplifying the equation (8) when  $w, w'$  are in between 1 and -1 then we get

$$Z = 1 + x^2 \cos \theta + 4/4 \cos \theta + x^4 / 2 \cos^2 \theta \quad (9)$$

when  $\theta$  is zero the equation (9) becomes

$$Z_{\theta=0} \approx 1 + x^2 + 3/4 x^4 \quad (10)$$

$$\text{Where } x^2 = (4\pi/\lambda)^2 R_g^2/3 \quad (11)$$

By discarding higher power raised values of  $\cos \theta$  and  $x$  in equation (9), we get

$$Z_{\theta} \approx 1 + x^2 \cos \theta \quad (12)$$

For the determination of the radius of gyration from above equations,  $Z$  determined for different angles are plotted against  $\cos \theta$ . In this way one may get a straight line in case of lower values of dissymmetries or a curve in case of higher values of dissymmetries. A straight<sup>9</sup> line can be drawn through that curve, which will be an approximate straight line of dissymmetry versus  $\cos \theta$  plot. The slope of these straight lines will be equal to  $x$ .

In case of higher values of dissymmetries i.e. when one gets a curve instead of a straight line by plotting dissymmetry versus  $\cos \theta$ , it is better to plot dissymmetry against  $\cos^2 \theta$  and extrapolate to zero to obtain dissymmetry at zero angle and hence  $x$  can be found from equation (10). In this way radius of gyration can be found without any supposition or approximation.

#### Experimental

The cellulose acetate investigated in this work was obtained from Ravi Rayon Ltd. Kala Shah Kaku, Lahore as solution in acetone.

#### Preparation of Sample

The acetone which was used as a solvent in this system, was of E, Merck brand and it was double distilled before use. Using this acetone a solution of higher concentration than the required one was prepared from the stock solution. The concentration of the solution was determined by drying a known volume and weight of that solution at 60-62°C. The other solutions were prepared by dilution method. In this way the following three concentration ranges were prepared and studied.

1.  $1.0 \times 10^{-4}$  -  $1.0 \times 10^{-3}$  g/ml. by an interval of  $1.0 \times 10^{-4}$  g/ml.

2.  $1.0 \times 10^{-3}$  -  $1.0 \times 10^{-2}$  g/ml. by an interval of  $1.0 \times 10^{-3}$  g/ml.

3.  $1.0 \times 10^{-2}$  -  $6.0 \times 10^{-2}$  g/ml. by an interval of  $1.0 \times 10^{-2}$  g/ml.

#### Dissymmetry measurements

As the commercially available polymer was contaminated by dust and microgels, the solutions were therefore filtered through millipore filters under nitrogen pressure. The filtration was carried out twice or thrice until we got reproducible results upto 0.04 dissymmetry values. The clarified solutions were subjected to light scattering. For the measurements of dissymmetry values Brice Phoenix light scattering instrument model DM 2000 was used. This instrument has a mercury arc lamp as a light source and two light filters which allow the light of 436 nm. and 546 nm. wave length. To measure the signal it is connected to light spot galvanometer. This galvanometer has different sensitivities which can be selected according to the requirement. The light scattering instrument is a double channel and therefore it is connected to a double channel recorder (Westronics) in place of galvanometer. In this way it was possible to get direct dissymmetry ratios. In case of galvanometer the dissymmetries were calculated by using the following equation<sup>23,24,25</sup>

$$Z_{\theta} = I_{\theta}/I(180-\theta)$$

$$Z_{\theta} = \frac{(FG_{\theta}/G_w)_{\text{solution}} (FG_{\theta}/G_w)_{\text{solvent}}}{(FG_{(180-\theta)}/G_w)_{\text{solution}} (FG_{(180-\theta)}/G_w)_{\text{solvent}}} \quad (13)$$

where  $Z_{\theta}$  is the dissymmetry measured at angle  $\theta$  with respect to incident light  $F$  is the product of the neutral filters used to reduce the intensity of the incident light  $G_{\theta}$ ,  $G_{(180-\theta)}$ ,  $G_w$  are the readings of galvanometer measured at angles  $\theta$ ,  $(180 - \theta)$  and zero degree respectively.

The dissymmetries of solutions were measured at wavelengths of 436 nm and 546 nm using cylindrical cell maintained at 25°C. In addition the dissymmetries of more dilute solutions were also measured. However due to less reproducibility and reliability results are not

reported here.

### Results and Discussion

The dissymetry calculated for various concentrations were plotted against concentration for a particular concentration range and angle  $\theta$ . From the slope of dissymetry versus concentration plots (not given) we observed that  $Z$  was not so much dependent upon concentration in the highest concentration range. At lower concentration ranges  $Z$  showed dependence on concentration though the difference was not much. However it was necessary to extrapolate to zero concentration. As the dissymetries were linear function of concentration in this system it was easy to get the value of  $Z$  (dissymetry) for zero concentration for a particular angle. These values of dissymetries are given in the table I, II and III for the first, second and third concentration ranges and for the two wave lengths.

The average radius of gyration is determined by using the equation (11) and (12) and the dissymetries values are plotted against  $\cos \theta$ . These are shown in figs. (1), (2) and (3). The graphs show curvature due to high values of dissymetries of the system under consideration.

Table I.

$Z_0$  values at different angles for first range  
( $1.0 \times 10^{-4}$  g/ml to  $1.0 \times 10^{-3}$  g/ml.) of concentration.

| Angle $\theta$ | $Z_0$ at angle $\theta$ |            |
|----------------|-------------------------|------------|
|                | at 436 nm.              | at 546 nm. |
| 45             | 5.5                     | 6.0        |
| 50             | 4.8                     | 5.1        |
| 55             | 3.9                     | 4.0        |
| 60             | 3.3                     | 3.0        |
| 65             | 2.8                     | 2.4        |
| 70             | 2.2                     | 2.0        |
| 75             | 1.8                     | 1.65       |
| 80             | 1.5                     | 1.5        |
| 85             | 1.2                     | 1.2        |
| 90             | 1.0                     | 1.0        |

Table II.

$Z_0$  values at different angles for second range  
( $1.0 \times 10^{-1}$  g/ml, to  $1.0 \times 10^{-2}$  g/ml.) of concentration.

| Angle $\theta$ | $Z_0$ at angle $\theta$ |            |
|----------------|-------------------------|------------|
|                | at 436 nm.              | at 546 nm. |
| 45             | 5.1                     | 5.7        |
| 50             | 4.3                     | 5.0        |
| 55             | 3.7                     | 4.1        |
| 60             | 3.2                     | 3.4        |
| 65             | 2.6                     | 2.6        |
| 70             | 2.2                     | 2.2        |
| 75             | 1.8                     | 1.8        |
| 80             | 1.5                     | 1.4        |
| 85             | 1.2                     | 1.2        |
| 90             | 1.0                     | 1.0        |

Table III.

$Z_0$  values at different angles for third range  
( $1.0 \times 10^{-2}$  to  $6.0 \times 10^{-2}$  g/ml) of concentration.

| Angle $\theta$ | $Z_0$ at angle $\theta$ |            |
|----------------|-------------------------|------------|
|                | at 436 nm.              | at 546 nm. |
| 45             | 4.8                     | 4.5        |
| 50             | 4.0                     | 3.9        |
| 55             | 3.5                     | 3.4        |
| 60             | 2.85                    | 2.8        |
| 65             | 2.3                     | 2.4        |
| 70             | 1.9                     | 2.0        |
| 75             | 1.6                     | 1.6        |
| 80             | 1.3                     | 1.3        |
| 85             | 1.2                     | 1.2        |
| 90             | 1.0                     | 1.0        |

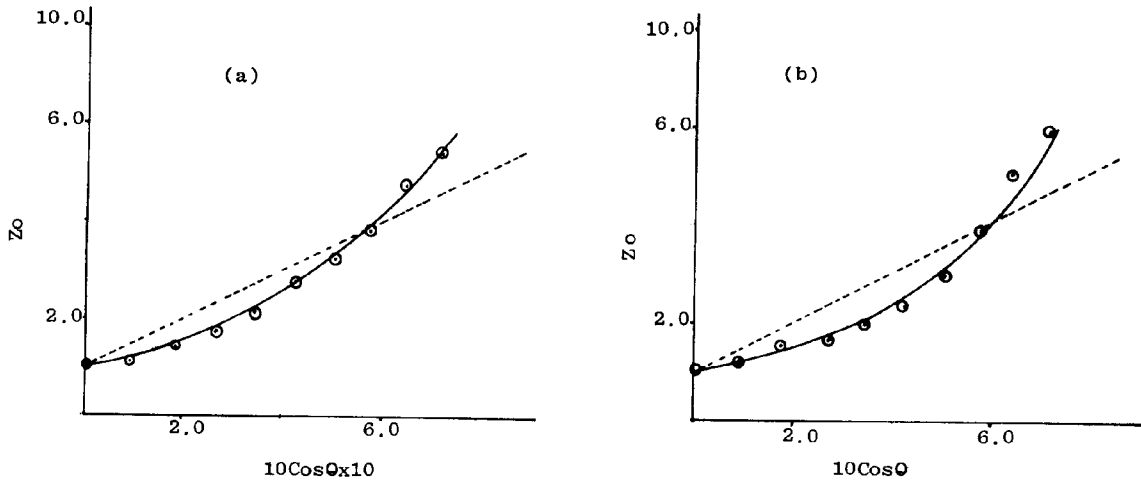


Fig. 1 (a,b). Plots of  $Z_O$  as a function of  $\text{Cos } \Theta$  for 1st range of concentration (a) at 436 nm, and (b) at 546 nm, wave length. Continuous curve is experimentally determined results of  $Z_O$  and broken line is the approximation of that as a straight line with slope equal to  $X^2 + \frac{1}{4} X^4$ .

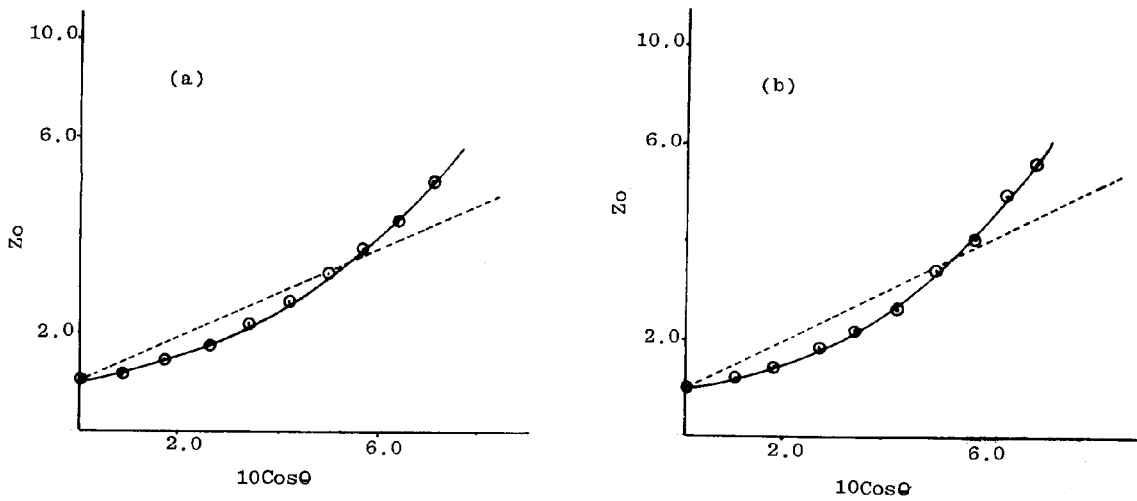


Fig. 2 (a,b). Plots of  $Z_O$  as a function of  $\text{Cos } \Theta$  for 2nd range of concentration (a) 436 nm. and (b) 546 nm. wave length. Continuous curve is the experimentally determined results of  $Z_O$  and broken line is the approximation of that as a straight line having slope equal to  $X^2 + \frac{1}{4} X^4$ .

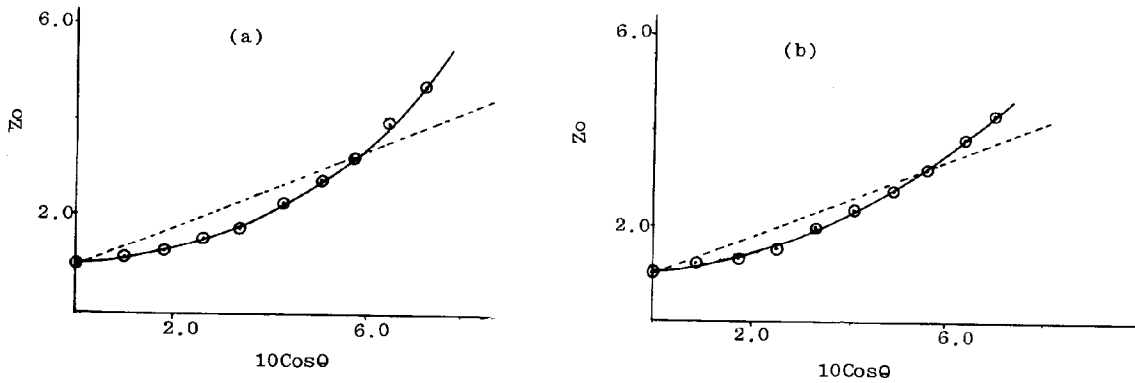


Fig. 3 (a,b). Plots of  $Z_O$  as a function of  $\text{Cos } \Theta$  for 3rd range of concentration (a) 436 nm. and (b) 546 nm. wave length continuous curve is the experimentally determined results of  $Z_O$  and broken line is the approximation of that as a straight line having slope equal to  $X^2 + \frac{1}{4} X^4$ .

Table IV.

Result obtained and calculated from the graphs of  $Z_0$  versus  $\cos \theta$  and  $Z_0$  versus  $\cos^2 \theta$  for 436 nm.

| S.No. | Concentration range No. | $Z \approx 1 + x^2 + 3/4 x^4$<br>$\theta \rightarrow 0$<br>$C \rightarrow 0$ | $x^2 + 1/4 x^4$ | $x^2$ | $R_g \text{ in } \text{\AA}^\circ$ |
|-------|-------------------------|--|-----------------|-------|------------------------------------|
| 1.    | Ist.                    | 10.0   | 4.91            | 2.861 | 1090                               |
| 2.    | 2nd.                    | 9.1  | 4.491           | 2.687 | 1056                               |
| 3.    | 3rd.                    | 8.2  | 4.068           | 2.503 | 1020                               |

Table V.

Results obtained and calculated from the graphs of  $Z_0$  versus  $\cos \theta$  and  $Z_0$  versus  $\cos^2 \theta$  for 546 nm.

| S.No. | Concentration range No. | $Z \approx 1 + x^2 + 3/4 x^4$<br>$\theta \rightarrow 0$<br>$C \rightarrow 0$ | $x^2 + 1/4 x^4$ | $x^2$ | $R_g \text{ in } \text{\AA}^\circ$ |
|-------|-------------------------|--|-----------------|-------|------------------------------------|
| 1.    | Ist.                    | 10.7   | 5.223           | 2.991 | 1396                               |
| 2.    | 2nd.                    | 10.3   | 5.045           | 2.917 | 1378                               |
| 3.    | 3rd.                    | 7.9  | 3.926           | 2.926 | 1261                               |

To overcome this difficulty the dotted line is drawn in every case to obtain a straight line the slope of which is equal to  $x^2$  (equation (11)).

For the utilization of equation (10) the dissymetry values for Zero concentration and other concentration ranges are plotted against  $\cos^2 \theta$  for each wave length. A straight line for each concentration ranges is obtained as shown in figs. 4,5 and 6. It is clear from these figures that it is easy to extrapolate for zero degree angle and to get dissymetry for zero angle, which means to get the  $R_g$  without interference. The results obtained in this way are given in tables, IV, V for different concentration ranges and wave lengths.

The results obtained in this way are compared with the results obtained by Zimm<sup>10,11</sup> plot. They are found to be the same within experimental error. The method used is easy to apply to any system and gives

accurate results. Also one can even confirm the shape of the polymer using this method, which is not possible to conclude by Zimm plot method. The other thing in this case is that there is no need of knowing the degree of dispersity.

It is clear from the figures that one can eliminate the error by analysing the results using equation (10) as compared to equation (12), particularly for large particles i.e. the particles having high dissymetry values.

The values for  $R_g$  in the tables IV and V, are higher for the 546 nm, wave length than for the 436 nm wave length. This shows that 546 nm is more effective and sensitive to higher molecular weight particle. The difference also arises from the polydispersity of the system<sup>18</sup>. These results also show variations in the  $R_g$  values with concentration.  $R_g$  has large value for lower concentration and smaller value for higher concentra-

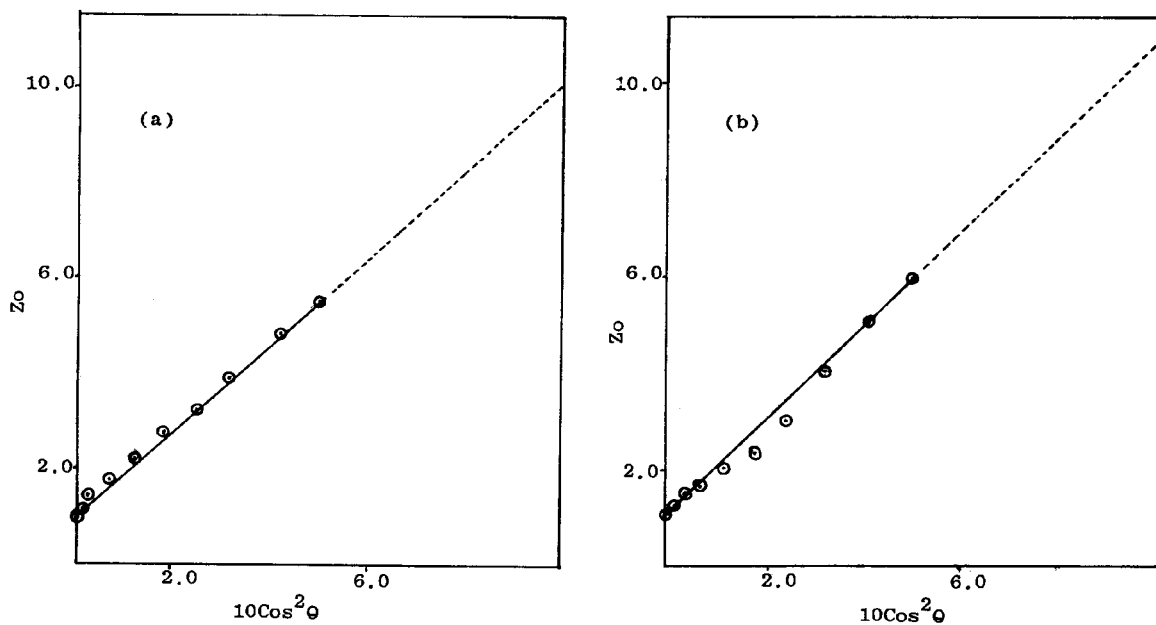


Fig. 4 (a,b). Plots of  $Z_0$  as a function of  $\text{Cos}^2\theta$  for 1st range of concentration and extrapolated to zero angle. (a) 436 nm. and (b) 546 nm. wave length.

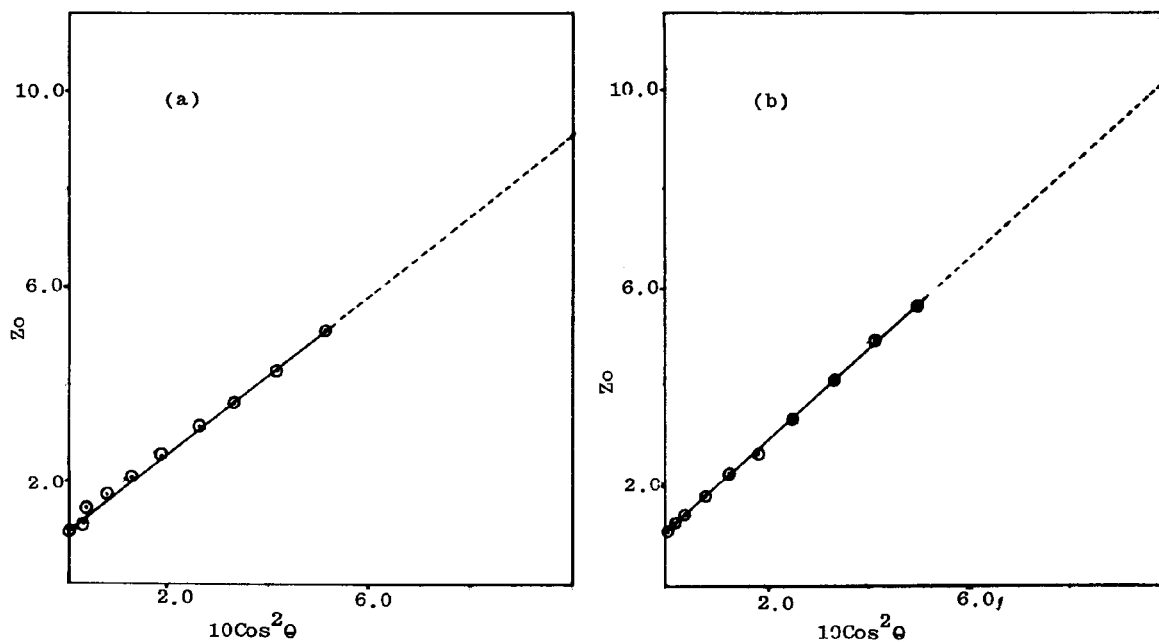


Fig. 5 (a,b). Plots of  $Z_0$  as a function  $\text{Cos}^2\theta$  and extrapolated to zero angle for 2nd range of concentration. (a) 436 nm. and (b) 546 nm. wave length.

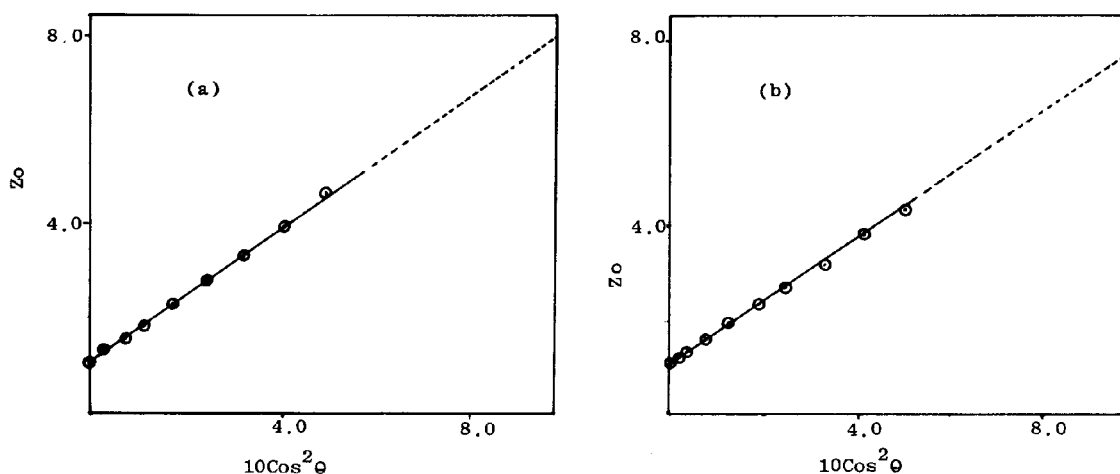


Fig. 6 (a,b). Plots of  $Z_0$  as a function of  $\text{Cos}^2 \theta$  and extrapolated to zero angle for 3rd range of concentration. (a) 436 nm. (b) 546 nm. wave length.

tion. This means that the molecules will be in the extended form in dilute solutions as compared to concentrated solutions. These results agree with the general behaviour of the polymer solvent system.

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#### References

1. R.S. Stein and P. Doty. *J.Am.Chem.Soc.* **68**, 159-167 (1946).
2. P. Doty and R.F. Steiner. *J.Chem.Phys.* **18**, 1211-20 (1950).
3. D. Cleverden; D. Laker and P.G. Smith. *J.Poly.Sci.* **17**, 133-5 (1955).
4. P. Debye and E.W. Ancher, *J.Phys. Chem.* **55**, 644 (1951).
5. P.M. Doty; B.H. Zimm; and H. Mark, *J.Chem. Phys.* **12**, 144-5 (1944).
6. B.A. Zimm; and P.M. Doty, *J.Chem. Phys.* **12**, 203-4 (1944).
7. N.K. Subramanian and S.R. Sivarajan, *Indian J. Phys.* **35**, 135-42 (1961).
8. Noor Ahmad and Musa Kaleem, *Pak.J.Sci. and Tech.* **1980** (Accepted for publication).
9. Y. Young; P.J. Missal; N.A. Mayor; G.B. Benedek and M.C. Carey. *J.Phys.Chem.* **82**, 1375 (1978).
10. B.H. Zimm. *J.Chem. Phys.* **16**, 1093-99 (1948).
11. B.H. Zimm. *J.Chem.Phys.* **16**, 1099-116 (1948).
12. J.W. Strutt (Lord Rayleigh), *Phil. Mag.* (4), **41**, 107,447 (1871).
13. M.B. Huggin, Light Scattering from polymer solutions, Academic Press London and New York (1972) p. 33-379.
14. W.H. Beattie and C.Booth. *J.Phys. Chem.* **64**, 696-97 (1960).
15. W.H. Beattie and C.Booth. *J.Poly.Sci.* **44**, 81-91 (1960).
16. L.T. Muns and F.W. Billmeyer, *J.Am.Chem.Soc.* **79**, 5079 (1977).
17. P.Doty and S.T. Stein. *J.Poly.Sci.* **31**, 763 (1948).
18. E. J. Meehan and W.H. Beattie. *J.Phys.Chem.* **64**, 1006 (1960).
19. T. Yukiko; and P. Robert. *J.Chem.Phys.* **51** (8) 3298-305 (1969).
20. P. Debye. *J. Applied Phys.* **15**, 338 (1944); *J.Phys. and Colloid Chem.* **51**, 18 (1947).
21. H.Benoit. *J.Poly.Sci.* **1**, 507 (1953).
22. A. Peterlin, *J.Poly.Sci.* **10**, 425 (1953).
23. Y. Tomimatsu and K.J.P. Palmer. *J.Phys. Chem.* **67**, 1720-22 (1963).
24. B.A. Brice; M.Halwer and R. Speiser. *J.Opt.Soc.* **40** (11) 768 (1950).
25. J.P. Kratochvil. *J. Colloid and Interface Sci.* **22**, 498-512 (1966).