Determination of surface tension, optical rotativity and refractive index of polymer polyvinyl alcohol PVA, $(\bar{M}_w = 1.25,000)$ in various solvents at different concentrations

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Abstract

Surface tension, Optical Rotativity and Refractive Index of Polymer PVA ($\bar{M}_w$=1,25,000) in various solvents like distilled water, N_aOH, KOH and Urea at different concentrations are measured, which enable us to know the interaction of the polymer molecules in these solvents.

Keywords: Surface tension, Optical Rotativity, Refractive Index.

Resumen

La Tensión Superficial, Rotación Óptica e Índice de Refracción de Polímero PVA (($\bar{M}_w$=1,25,000) en diversos solventes como el agua destilada, N_aOH, KOH y Urea a diferentes concentraciones son medidos, lo que nos permite conocer la interacción de las moléculas del polímero en estos solventes.

Palabras clave: Tensión Superficial, Rotación Óptica, Índice de Refracción.

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I. INTRODUCTION

Solvation dynamics has been the focus of intense research activities for the past few years. Experimental and theoretical studies have given rise to renewed interest in the field. Measurement of some physical properties like viscosity(η), density (ρ), surface tension (T), Optical Rotativity (S), Refractive Index (μ) provide insight into the intermolecular arrangements of the components in solutions, which are able to throw light on the properties of polymer PVA.

II. THEORY

i) Surface Tension: The surface tension T of liquid [1] is given by T = ½ρgr$\left(h + \frac{1}{3}r\right)$.

Where ρ represents the density of the liquid, and g is the accerelation due to gravity.

Jurin's law states that, the product of the effective height H$\left(= h + \frac{r}{3}\right)$ of the liquid coloumn and radius r of the capillary tube is a constant. A plot of $\frac{1}{r}$ against H is a straight line. By using the value of rH $\left(where\ H = h + \frac{r}{3}\right)$ from this plot and knowing the other physical parameters, the surface tension T is determined from Eq. (1).

ii) Optical Rotativity: The angle of rotation θ of the plane of polarization, for a given wavelength λ, is directly proportional to the length *l* of the active substance traversed. For solutions, the angle of rotation θ for a given path length is proportional to the concentration of solution [2].

Specific rotation(S) of an optically active substance at a given temperature t and for a given wavelength λ of light is defined as the rotation (in degrees) produced by one decimeter length of the substance in solution when its concentration is 1g/cc.

$$[S]_\lambda^t = \frac{\theta}{l\times C} = \frac{Rotational\ in\ degrees}{Length\ in\ decimeter\times concentration\ in\ g/cc}. \quad (1)$$

If *l* is expressed in centimeter, then

$$[S]_{\lambda}^{t} = \frac{10\theta}{lc}. \tag{2}$$

For a given $l, \frac{\theta}{c}$ can be obtained from the plot and specific rotation of given solvent and polymer solution is determined with help of Eq. (2).

iii) Refractive Index: The ratio of the image to object distance for paraxial rays is just equal to the ratio of the indices of refraction. If the object is in a denser medium, then the refractive index of the denser medium with respect to first (rarer medium) is

$$\mu = \frac{Velocity\ of\ light\ in\ free\ space}{Velocity\ of\ light\ in\ medium}.$$

In our experiment, we have used the expression

$$\mu = \frac{Real\ depth}{Apparent\ depth}. \tag{3}$$

III. EXPERIMENTAL

A. Requisites

a) Polymer: The polymer PVA ($\bar{M}_w = 1{,}25{,}000$) is used as such without any further purification.

b) Solvents: The solvents such as aqueous solutions of NaOH, KOH, Urea are BDH (AR) grade and used as such throughout the experiment. A freshly prepared solutions of samples were prepared with solvents distilled water, NaOH, KOH, Urea at different concentrations.

c) For measurement of surface tension, an arrangement containing parallel capillary tubes on a glass plate, a pointer attached to the glass plate, a trough containing experimental liquid and a travelling microscope.

i) For measurement of specific rotation, Laurent half-shade polarimeter with a Sodium Vapour Lamp (light source) is used.

j) For Refractive Index measurement, a beaker containing experimental liquid (solvent and polymer solution), lycopodium powder and a travelling microscope are used.

B. Method

(i) Surface Tension: Capillary tubes of uniform bores of different sizes are cleaned, fixed parallel to each other on a strip of glass plate by soft wax. A clean needle with pointed ends is also fixed to the glass strip. Clean glass beaker filled with experimental liquid almost completely, is placed on a horizontal platform, so that the tubes remain vertical with lower ends immersed in the liquid, while the lower end of the needle just tourches the liquid surface. With the help of a travelling microscope, the height of liquid columns were recorded. Then tubes were broken at the position of liquid meniscus and diameter of tubes were measured.

(ii) Specific Rotation: Reading on circular scale of Laurent Half-shade Polarimeter (source N_a Vapour lamp) was recorded, when the tube was filled with distilled water (two halves of field of view were equally dark). Then the tube was filled with experimental liquid and placed in position. The circular scale was adjusted, till the two halves were again equally dark. The difference of the two readings gave the rotation of plane of polarization.

(iii) Refractive Index: The experimental liquid was kept in a clean beaker and its apparent depth was noted. Then a pinch of lycopodium powder was sprinkled on the surface of liquid and its real depth was measured. Here all the measurements were taken in daylight. In measuring refractive index of N_aOH and KOH solutions, fine cork powder was used as lycopodium powder is readily dissolved in the above mentioned solutions.

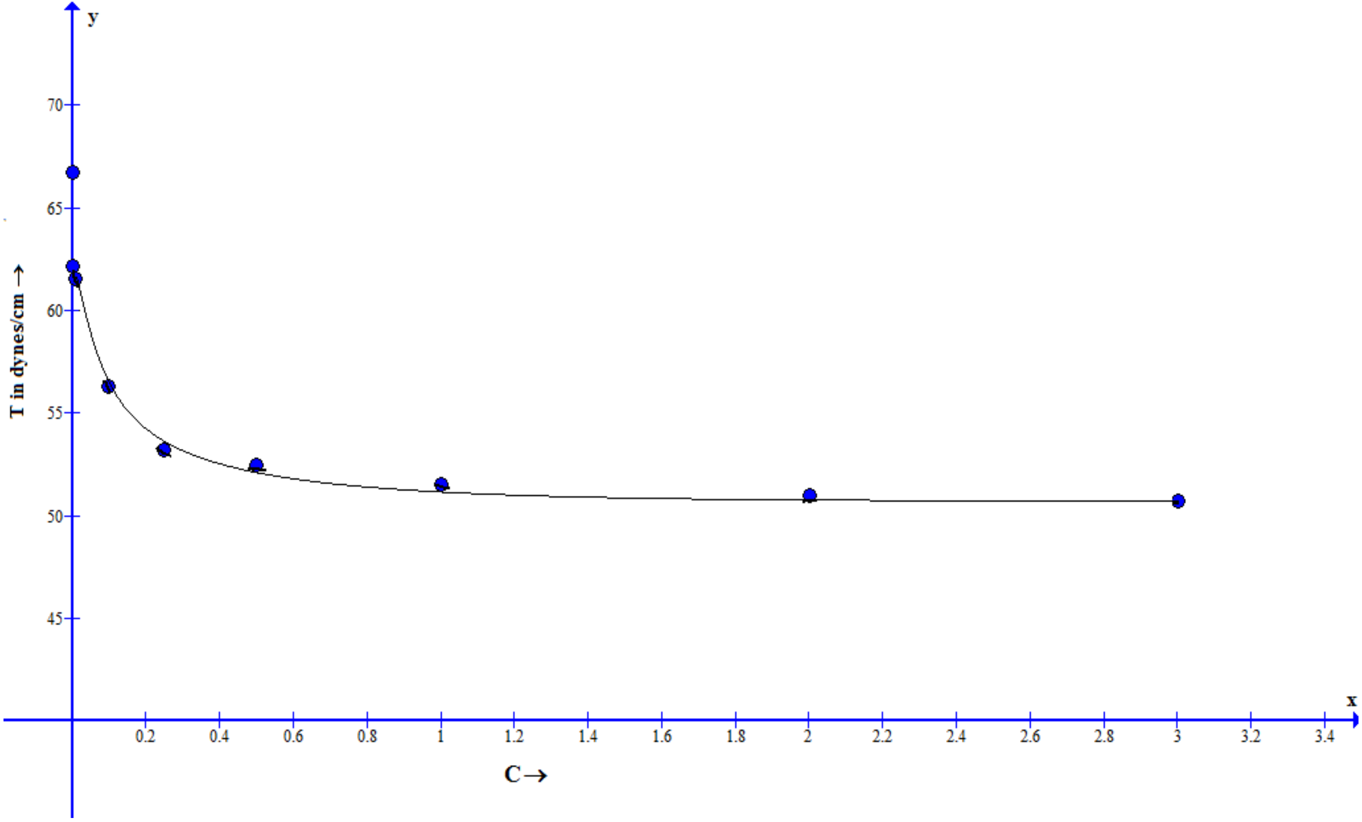

FIGURE 1. Surface Tension T ~ Concentration C Plot for 1% PVA (Mw=1,25,000) solution at various concentrations.

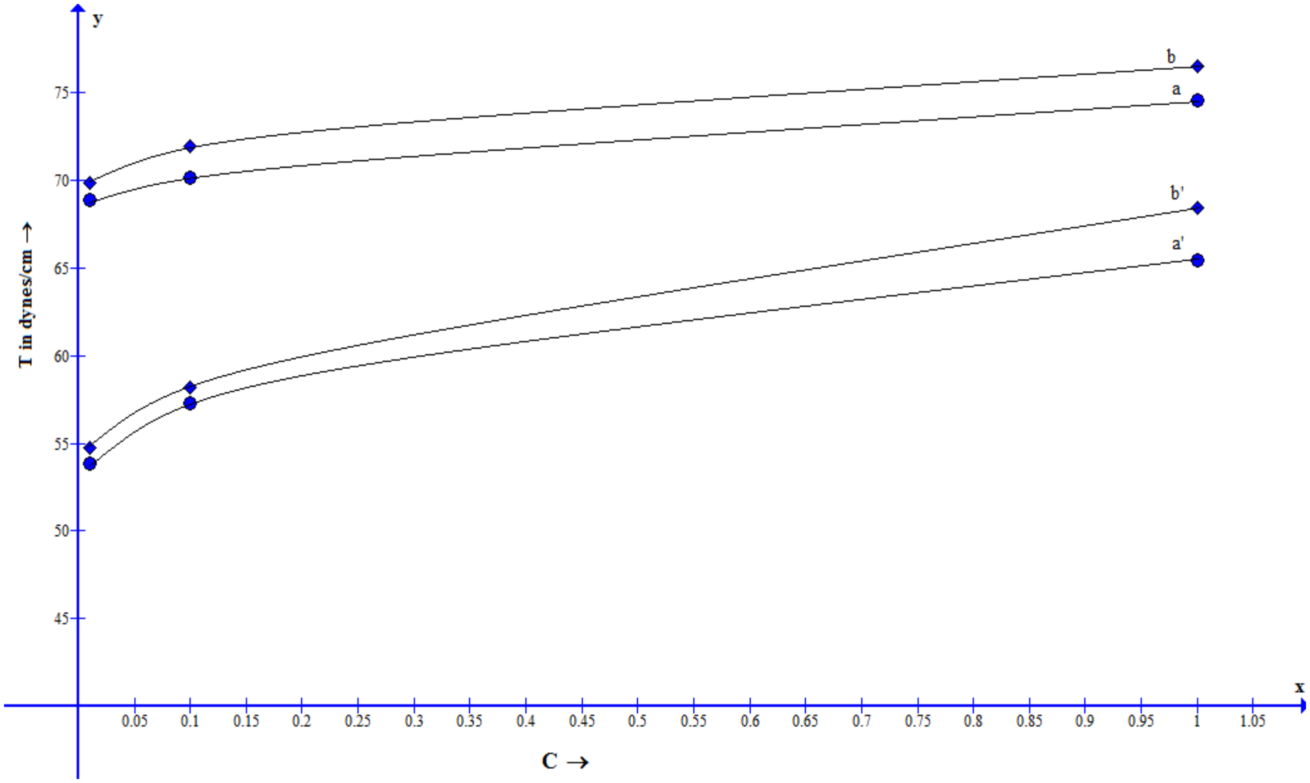

FIGURE 2. Surface Tension T ~ Concentration C Plot for solvents NaOH, KOH (a, b) and 1% PVA (Mw=1,25,000) solutions in above solvents (a', b') at various concentrations.

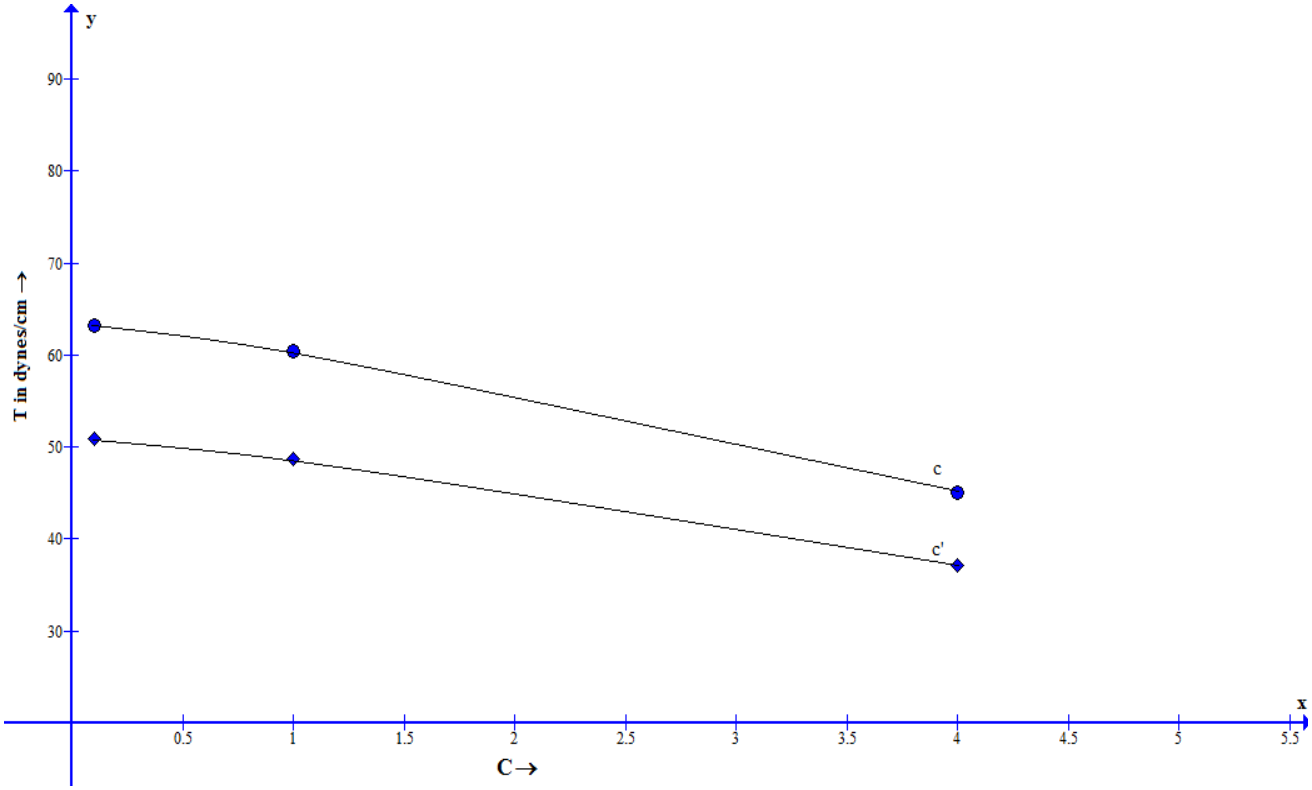

FIGURE 3. Surface Tension T ~ Concentration C Plot for solvent Urea(c) and 1% PVA (Mw=1,25,000) solution in above solvent (c') at various concentrations.

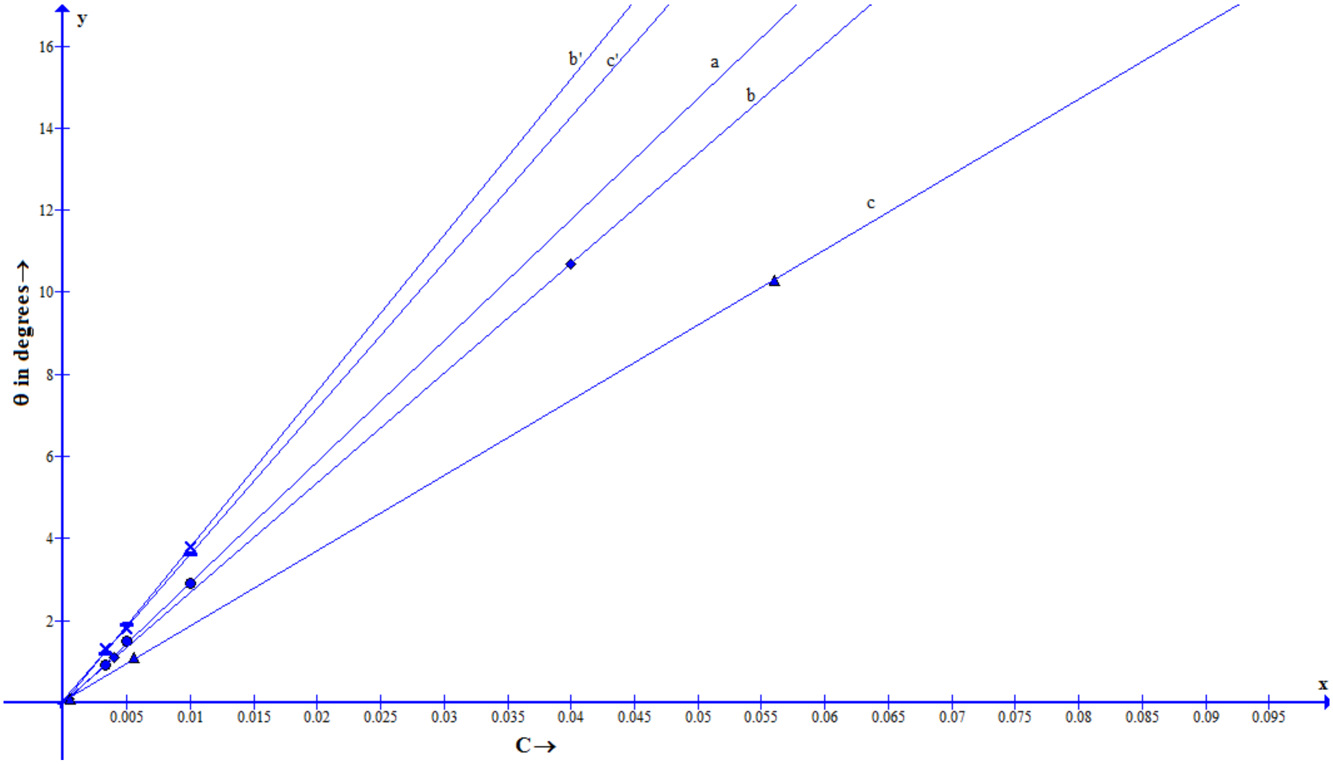

FIGURE 4. Rotation of plane of Polarization θ ~ Concentration C Plot for solvents NaOH, KOH (b, c) and 1% PVA (Mw=1,25,000) solution in solvents distilled water, NaOH, KOH (a, b', c') at various concentrations.

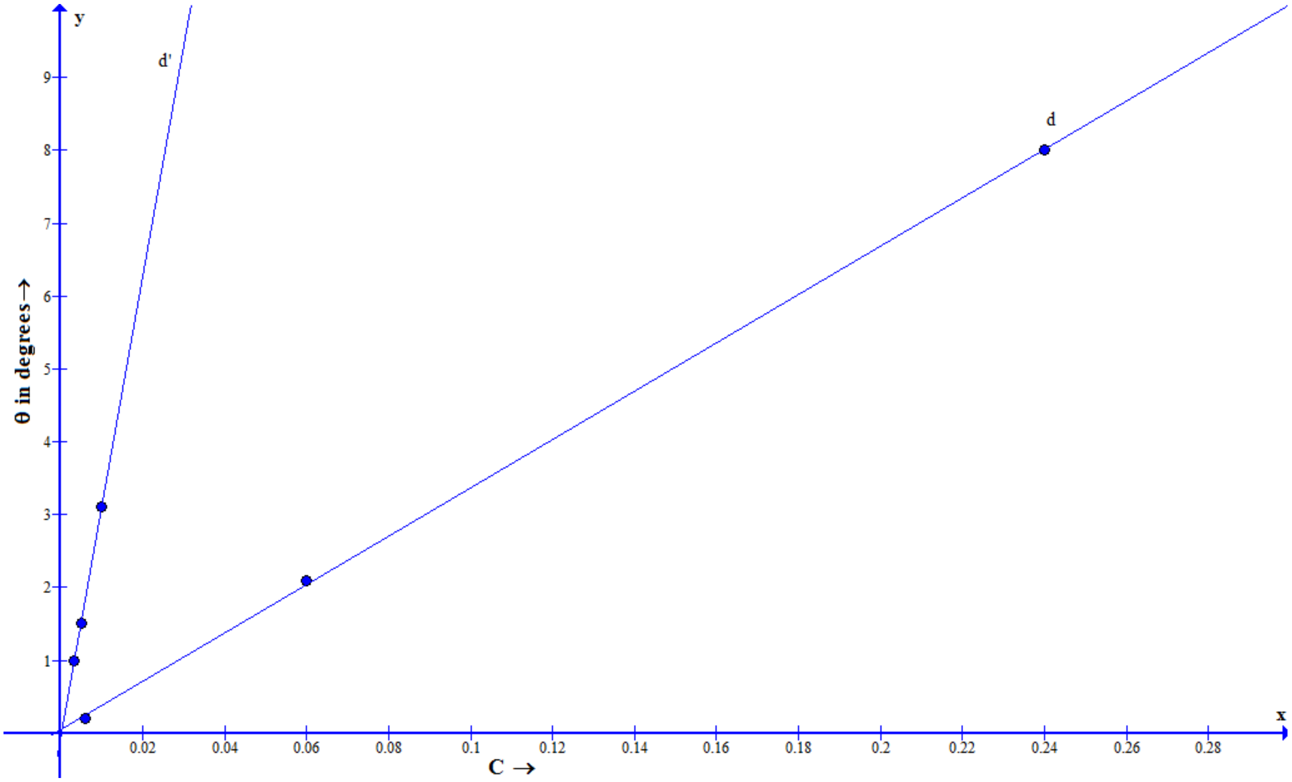

FIGURE 5. Rotation of plane of Polarization θ ~ Concentration C plot for solvent Urea (d) and that of 1% PVA (Mw=1,25,000) solution in above solvent (d') at various concentrations.

IV. RESULT AND DISCUSSION

i. Surface tension of a system is governed by usual thermodynamical variables and primarily by the chemical nature of the components present in the surface phase. In our experiment, we have determined surface tension using Jurin’s law at temp. 27^0C. Surface tension of distilled water is reduced (T = 66.71 dynes/cm). It is because, distilled water during its preparation is likely to have a small traces of grease, which lowers the surface tension value [3]. Surface tension of PVA solutions (solvent distilled water) of different concentration are recorded and shown in Fig. 1

As concentration of PVA solution increases, its surface tension value decreases. PVA has the capability of H-bonding with its solvent (distilled water). For PVA solution, the solute (PVA) and water molecules exert attraction on their immediate neighbours. Because of the difference of interaction, the fields of attractive forces exerted by PVA molecules will be different from those exerted by water molecules PVA molecules remain at a higher free energy state and always has a tendency to migrate to surface (*i.e.* at low free energy state). The accumulation of PVA on the surface results in excess positive surface tension values and hence the surface tension of PVA solution is decreased. With the increase in concentration of PVA, the surface excess value increases and hence the surface tension trend is reversed. It is observed that, at lower concentration, the decrease is very sharp and continues to fall slowly as concentration increases. At lower concentration, the attraction among the water molecules results in a water-pulling effect, which is more than that in a PVA solution of higher concentration. Hence, an increase in surface excess value results in lower concentration (*i.e.* sharp decrease in surface tension) [4, 5].

Surface tension value of PVA solution in solvents NaOH, KOH and Urea are measured. We observe that, in case of solvents NaOH and KOH, surface tension increases and in case of solvent Urea, the surface tension decreases

TABLE I. Rotation of plane of polarization of solvents distilled water, NaOH, KOH, Urea and that of 1% PVA solutions in above solvents at various concentrations.

No. of Observations	**Concentration of solution C(gm/cc)**	**Reading on the circular scale, when two halves are equally dark with solution in tube; θ_2 in degrees**	**Rotation of plane of polarization $\theta=(\theta_1-\theta_2)$ In degress**	$\frac{\theta}{c}$ $\boldsymbol{from\ graph}$	**S from graph**
1.Distilled Water:					
	-	358.8	0	-	-
2. 1% PVA in distilled water:					
	0.01 0.005 0.00333	1.7 0.3 359.7	2.9 1.5 0.9	‘a’ 295.277	144.0376
3. Solvent NaOH (Base liquid distilled water; $\theta_1=358.8^0$)					
	(1N NaOH) 0.04 (0.1N NaOH) 0.004 (0.01NaOH) 0.0004	9.5 359.9 358.9	10.7 1.1 0.1	‘b’ 267.267	130.3741
4. 1% PVA in NaOH (Base liquid 1N NaOH; $\theta1=9.5^0$)					
	0.01 0.005 0.00333	13.3 11.3 10.8	3.8 1.8 1.3	‘b’’ 380.615	185.6659
5. Solvent KOH (Base liquid distilled water; $\theta_1=358.8^0$)					
	(1N KOH) 0.056 (0.1N KOH) 0.0056 (0.01N KOH) 0.00056	9.1 359.9 358.9	10.3 1.1 0.1	‘c’ 183.398	89.4624
6. 1% PVA in KOH (Base liquid 1N KOH; $\theta_1=9.1^0$)					
	0.01 0.005 0.00333	12.7 11.0 10.3	3.6 1.9 1.2	‘c’’ 355.254	173.2946
7. Solvent Urea (Base liquid distilled water; $\theta_1=358.8^0$)					
	(4M Urea) 0.24 (1M Urea) 0.06 (0.1M Urea) 0.006	6.8 0.9 359.0	8.0 2.1 0.2	‘d’ 33.193	16.1917
8. 1% PVA in 4m Urea (Base liquid 4m Urea; $\theta=6.8^0$)					
	0.01 0.005 0.00333	9.9 8.3 7.8	3.1 1.5 1.0	‘d’’ 316.0	154.1463

Observations: L. C. of vernier = 0.1 degree, *l* = 20.5cm.
Reading on circular scale, when two halves of field of view are equally dark, when the tube is filled with distilled water; $\theta = 358.8^0$.

TABLE II. Refractive Index of solvents distilled water, $\mathrm{N_aOH}$, KOH Urea and that of 1% PVA($\bar{M}_w = 1{,}25{,}000$) solutions in above solvents at various concentrations.

Solvents	*Refractive Index of solvents*			*Refractive Index of 1% PVA solutions*		
Distilled water	1.32727			1.36123		
	Concentration of solvents			*Concentration of 1% PVA solutions*		
	0.01N	0.1N	1.0N	PVA in 0.01N solvent	PVA in 0.1N solvent	PVA in 1.0N solvent
NaOH	1.33333	1.33696	1.33877	1.33875	1.34102	1.34937
KOH	1.33675	1.33912	1.34283	1.34001	1.34353	1.35019
NaOH	0.1M	1.0M	4.0M	PVA in 0.1M Urea	PVA in 1.0M Urea	PVA in 4.0M Urea
	1.33999	1.34211	1.37422	1.35194	1.36102	1.39351

It is expected, because inorganic substances (NaOH, KOH) dissolved in a liquid increases surface tension, whereas organic substance (Urea) decreases the surface tension value. But when 1% PVA solution prepared with the above solvents are taken, the surface tension values are lowered (as already described). The variation of surface tension of solvents (NaOH, KOH, Urea) and that of PVA solution at various concentrations are shown in Fig. 2 and Fig. 3.

ii) The rotation of plane of polarization of solvents (distilled water, NaOH, KOH, Urea) and that of PVA solutions at various concentrations are recorded in Table I. The specific rotation values for above mentioned solvents and solutions are calculated graphically by taking the slope of $\theta \sim C$ plot (Fig. 4 and Fig. 5).

iii) Here, we observe that solvents NaOH, KOH and Urea are optically active. The reason is as follows; each molecule of a liquid may be thought of as a small crystal with an optic axis along which plane-polarised light is rotated. Since in a liquid, the molecules are oriented at random, the observed rotation is an average effect of all molecules and therefore the same in any direction through the liquid. The random orientation of molecules does not affect the rotatory effect, since each molecule has a screw like structure and is same from which end it is viewed.

iv) In case of PVA solutions (in solvents distilled water, NaOH, KOH and Urea at various concentrations), the helical structure of PVA is the cause of rotation of linearly polarized light [6]. As light travels down the helical path the direction of vibration gets changed. As solvents (except distilled water) as well as polymer PVA are optically active, the specific rotation of polymer solution is more in comparison to that of the solvent (base liquid). All the observed rotations are dextrorotatory.

v) The refractive index of solvents (distilled water, NaOH, KOH, Urea) and solutions (PVA in above mentioned solvents) at various concentrations are measured and recorded in Table II. High values of refractive index of polymer solutions may have some connection with their viscosity. In our earlier paper [7], we have determined the intrinsic viscosity of polymer solutions. We observe that the refractive index values of polymer solutions follow the same trend as viscosity values.

V. CONCLUSION

The study of surface tension of polymer is quite promising as it is the exception of other surface active agents. It explains the microstructure of polymermolecules. Optical rotativily describes the helicily nature of PVA molecules and confirms long-chain structure of PVA. Refractive index of polymer solutions depend upon the wavelength of radiation used. But observations for other radiations (except day light) could not be taken due to lack of proper laboratory arrangements.

VI. ACKNOWLEDGEMENT

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