

Variations in the Refractive Index Increments of Cellulose Acetate in Acetone with Respect to Concentration and Temperature

NOOR AHMAD AND MUSA KALEEM

*National Centre of Excellence in Physical Chemistry,
University of Peshawar
Peshawar, Pakistan*

(Received 22nd March, 1983)

Summary: In order to make use of light scattering technique for the determination of molecular weight distribution etc of polymers it is necessary to know the refractive index increment of the system. In this work we have determined the refractive index increment of cellulose acetate in acetone solution. The concentration of the polymer was varied from 1.0×10^{-5} g/ml to 1.0×10^{-1} g/ml. For this purpose two wavelengths of incident light were used. From this data the specific refractive index increment of the system is also determined. To characterize the polymer at different temperatures, we have determined the same parameter at different temperatures ($10^{\circ}\text{C} - 55^{\circ}\text{C}$) for three different concentrations and making use of three wavelengths of incident light.

Introduction

The refractive index of the solution is related to the polarizability (α) of the solution by the following equation [1]

$$n^2 - n_0^2 = 4\pi N \alpha \quad (1)$$

and

$$n^2 - n_0^2 = 2n_0 (dn/dc)c \quad (2)$$

where n, n_0 are the refractive indices of the solute and solvent respectively dn/dc is the refractive index increment; c is the concentration of the solution and N is the number of molecules per ml. As the polarizability of the solution is dependent upon concentration, temperature, pressure, wave length of the light used for measurements and solvent, so dn/dc is also dependent upon these factors. It varies [2,3,4] as the concentration of the sample varies in a particular solvent. It increases or decreases [3] with the

increase in concentration. Therefore it is necessary to find out the refractive index increment of every polymer for different concentrations and at different temperatures.

Though cellulose acetate is a very useful polymer but its refractive index increment is known only for its three different fractions at a constant temperature in acetone [5]. Therefore in this work the cellulose acetate which was obtained from Ravi rayon Ltd. Kala Shah Kaku, Lahore, Pakistan is investigated with respect to its refractive index increment.

The refractive index increment of cellulose acetate in acetone is determined by varying the concentration from 1.0×10^{-5} g/ml. to 0.1 g/ml at regular intervals using two different wavelengths of light. The specific refractive index increment is found by extrapolation

method. The refractive index increment of this polymer is also determined at different temperatures (10°C-55°C) and three different wavelengths of incident light. In this way the effect of concentration and temperature upon refractive index increment of system is studied.

Experimental

A known concentration of cellulose acetate was made by dissolving the cellulose acetate in acetone. The acetone used was of E. Merck type and was doubly distilled before use. The concentration of the solutions was determined by drying the known volume of the solution at 60°C-62°C. To study refractive index increment as a function of concentration, the following four different concentration ranges were prepared.

i) 1.0×10^{-5} g/ml - 1.0×10^{-4} g/ml

by an interval of 1.0×10^{-5} g/ml

ii) 1.0×10^{-4} g/ml - 1.0×10^{-3} g/ml

by an interval of 1.0×10^{-4} g/ml

iii) 1.0×10^{-3} g/ml - 1.0×10^{-2} g/ml

by an interval of 1.0×10^{-3} g/ml

iv) 1.0×10^{-2} g/ml - 1.0×10^{-1} g/ml

by an interval of 1.0×10^{-2} g/ml

The measurements were made at 25°C.

For the effect of temperature upon refractive index increment, three different concentrations (0.06%, 0.60% and 1.61%) were used. The temperature variations were from 10°C to 55°C.

The refractive index increments were determined using Brice Phoenix Differential Refractometer. The optical system of this instrument is composed of light source (mercury arc), condensing and collimating lenses, slits to control the light, telescope and eye piece lens. The various filters of light allow the light of only 436 nm and 546 nm wave length. To get light of 632 nm wave length, we introduced another filter allowing the light of the required wave length. To keep the required temperature constant the measuring cell is housed in a metal jacket, through which thermostated water is circulated. The instrument was calibrated using NaCl solution in water and in this way the instrumental constant was determined.

The refractive index increment was measured for all the four ranges of concentration. The cell was properly stoppered to stop evaporation. The temperature was varied from 10°C to 55°C with an interval of 5°. To minimize the temperature variations in the cell and to get the required temperature more quickly, the length of the tubes (circulating the water) was reduced, the tubes and the cell jacket were thoroughly insulated from the surrounding by rolling asbestos threads around them. The solutions were kept at the required temperature for at least 20 minutes to assure the attainment of the temperature before measurement. The measurements were made at 436 nm, 546 nm and 632 nm wave length of incident light.

Results and Discussion

The refractive index increment ($\Delta n/c$) values obtained for four different concentration ranges are plotted against concentration for

every range and for both the wave lengths of light in figures 1 and 2. These figures show that the refractive index increment are linearly dependent upon concentration of the polymer as the equation (3) shows [3].

$$\Delta n/c = a_1 + a_2 c \quad (3)$$

where a_1 is the intercept and is called specific refractive index increment of the polymer and a_2 is the slope of the lines showing the dependence of $\Delta n/c$ upon concentration. The values of a_1 and a_2 obtained in this way are given in the table 1. The results show that $\Delta n/c$ values increase as the concentration of the polymer decreases (figure 1 and 2). This means the more dilute the solutions, higher the values of $\Delta n/c$ are observed. The change in $\Delta n/c$ is different for different range of concentration which is clear from the a_2 or $d(\Delta n/c)/dc$ values given in the table 1. a_2 values are higher

for lower range of concentration and lowest for fourth. These results show that the dependence of $\Delta n/c$ upon concentration becomes more significant in dilute to the increase of solubility/solvent of polymers having higher molecular weight (in dilute solutions), as the molecular weight in a homologous series increase [3,6,7] the refractive index increment increases. Moreover if we consider the equations (4,5) relating refractive index increment to the polarizability [1] and specific volume [3].

$$2 N \alpha = n_o (dn/dc) c \quad (4)$$

$$v = V_2 (n_2 - n_o) \quad (5)$$

then it can be well explained.

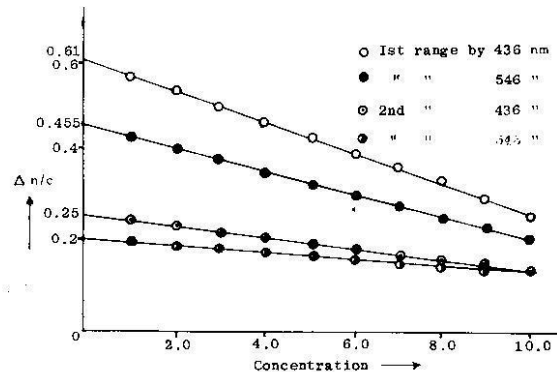


Fig.1: $\Delta n/c$ versus conc. $g/ml \times 10^3$ where $x = 5,4$ as range 1st, 2nd.

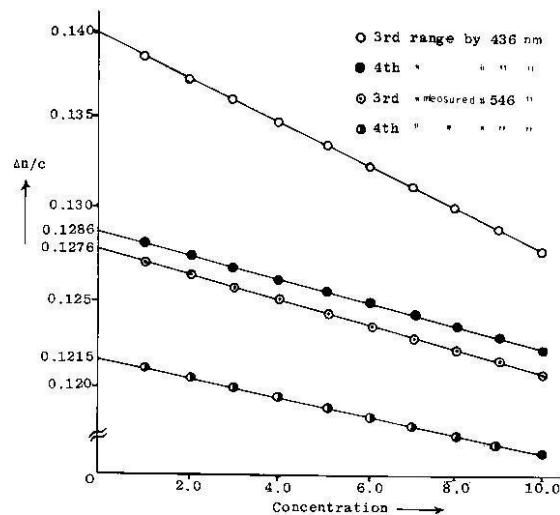


Fig.2: $\Delta n/c$ versus conc. $g/ml \times 10^3$ where $x = 3,2$ for as range 3rd, 4th.

Table-1: Values of $\Delta n/c$ when c approaches to zero and a_2 for all the four concentration ranges and for both the wavelengths of light

Wave-length	436 nm		546 nm	
	Conc. range No.	$v = a_1$ (ml/g)	$v = a_1$ (ml/g.)	a_2
1st	0.61	3.6×10^3	0.455	2.5×10^3
2nd	0.25	1.111×10^2	0.200	73.0
3rd	0.140	1.90	0.1276	0.66
4th	0.1286	0.061	0.01215	0.051

In case of dilute solutions the less entanglement between the polymer molecules will take place and the polymer molecules will be more in stretched form. Due to this reason they will show greater dipole-moment and hence higher polarizability, which means higher value of refractive index increment. On the other hand the polymer will be more solvated in dilute solutions and will show higher values of specific volume (V_2) and hence higher value

of specific refractive index increment in dilute solutions and vice-versa. The specific refractive index increment, which is defined as [3], the refractive index increment of the system when concentration approaches to zero measured at constant temperature (T), pressure (P) and wave length (λ_0). It can be mathematically written as

$$v = \lim_{c \rightarrow 0} (dn/dc) \quad (6)$$

v is obtained by extrapolating the plots of $\Delta n/c$ versus concentration upto zero concentration and is given in table 1 for all the four concentration ranges. These values are higher for lower concentration ranges and vice-versa, which is expected from equation (5). The Table 1 also provides the dependence of v upon wavelength of light used for the measurement. These values are higher for shorter wavelength of incident light. This difference decreases as the concentration of the system is increased or higher the v values greater is the difference. This difference can be explained by the equation (7) relating the specific volume of the polymer (V_2), refractive index of the solvent (n_0) to the values measured by using light of wavelength of λ'_0 and λ''_0 [3].

$$v \lambda'_0 - v \lambda''_0 = v_2 \left[[(n_2) \chi'_0 - (n_2) \chi''_0] - [(n_0) \chi'_0 - (n_0) \chi''_0] \right] \quad (7)$$

This equation shows that the difference is due to the different results obtained for n_2 and n_0 measured by two different wavelength as V_2 is independent of wavelengths of light used for measurement. Such type of differences are confirmed [3,7,8].

The $\Delta n/c$ values measured at difference temperatures for the three different concentrations are plotted against temperatures in figure 3,4, and 5. The slopes of all these lines are calculated and given in the table II, which provide the dependence of $\Delta n/c$ upon temperature for diffe-

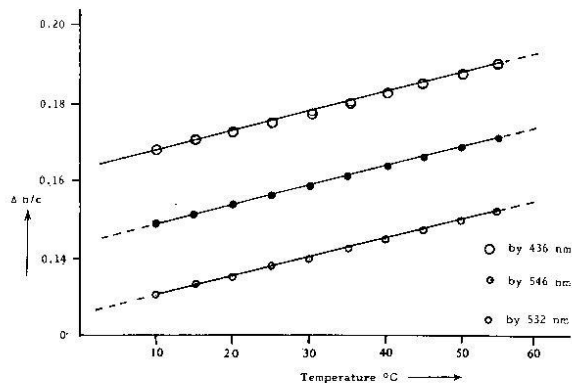


Fig.3: $\Delta n/c$ versus temperature for 0.06% conc.

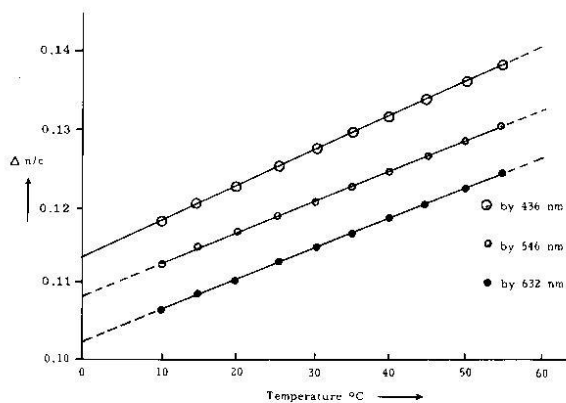


Fig.4 $\Delta n/c$ versus temperature for the conc. 0.60%

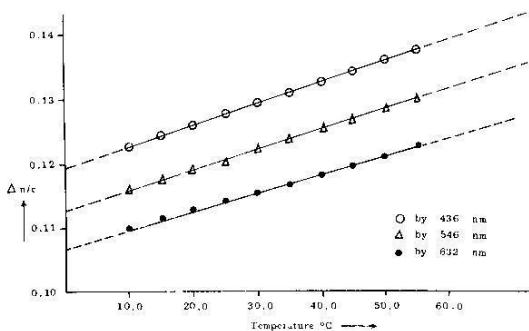
Fig. 5: $\Delta n/c$ versus temperature for concn. 1.61 %.

Table-2: Values of slopes of $\Delta n/c$ versus temperature for the three different concentrations, and for three wave lengths.

Wave-length Conc. %	$d(dn/dc)/dT \times 10^4$ ($\text{ml g}^{-1} \text{ deg.}^{-1}$)		
	436 nm	546 nm	632 nm
0.061	5.10	4.91	4.82
0.60	4.52	4.01	3.85
1.61	3.28	2.70	3.125

rent concentration wavelengths of incident lights. This table shows that the dependence of $\Delta n/c$ upon temperature is different in case of different wave length of incident light used and the slopes obtained are in the range of already available values in the literature [3,9]. The figures show that the refractive index increment increases in all cases when then temperature is raised. This increase may be due to the following reasons (i) Increase of solvation power of solvent (ii) Due to different effect of temperature upon solvent, solute and setting of new equilibrium at every temperature (iii) Increase in specific volume of the polymer. For quantitative analysis of refractive index increment upon temperature, it is necessary to concentrate

upon the table II. This table shows that the slope is higher for lower concentration and vice-versa. Similarly this values is less for longer wave length of incident light (for a particular concentration), except for the highest concentration, in which the case is little bit different.

Acknowledgement

The financial support of Pakistan Science Foundation is gratefully acknowledged.

Reference

1. C.Tanford Physical Chemistry of Macromolecules, John Wiley & Sons, Inc. New York 1961.
2. W.Heller, *J.Polymer.Sci.Pt. A.3(6)* 2367 (1965)
3. M.B.Huglin, Light Scattering from Polymer Solution, Academic Press, London and New York, (1972)
4. N.Ahmad and S.Ali, *J.Colloid, and Polymer Sci.*, **256**, 1085 (1978)
5. R.Stein and P.Doty, *J.Amer.Chem.Soc.*, **2(68)** 159 (1946)
6. J.K.Partington, *An Advanced Treatise on Physical Chemistry, Vol.4, Longmans, (1962)*
7. N.Ahmad and M.Kaleem; *Presented in Polymer Science Symposium held at Peshawar University, Pakistan 1982 and submitted for publication*
8. H.Yamakawa, *Modern Theory of Polymer Solutions, Harper and Row Publisher New York, (1971)*
9. J.H.O. Mara and D.Mc Intyre, *J.Physical Chemistry*, **63** 1435 (1959)