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TEMPERATURE DEPENDENCE OF THE REFRACTIVE INDEX INCREMENT OF CELLULOSE ACETATE IN ACETONE SOLUTION

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The refractive index increments of cellulose acetate in acetone are determined for three different concentrations and at ten different temperatures, using light of three different wave lengths. These are determined using Brice Phoenix Differential Refractometer. The values of slopes of the plots of refractive index increments versus temperature are in the range of $(2.70 \times 10^{-4}$ to 6.32×10^{-4} ml.g.$^{-1}$) deg.$^{-1}$) and are in agreement with the values quoted for general case. These values decrease withthe increase in concentration as from good to a poor solvent.

INTRODUCTION

Molecular weihgt [1–4] and molecular weight distribution of polymers are related to the mechanical and physical properties of the polymer, through a general equation,

$$\text{Property blend} = \Sigma_i w_i p_i / \Sigma_i w_i \quad \ldots\ldots\ldots (1)$$

where w_i is the weight of the molecular species with a mechanical property p_i.

To find the molecular weight and molecular weight distribution, by light scattering which is one of the molecular specific [5] method, the following equation is used,

$$Hc/\tau = 1/M + 2B_c + \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where

$$H = 32\ \lambda^3 n_o^2 .\ (dn/dc)^2 / (3 N \lambda^4) \ldots\ldots\ldots\ldots (3)$$

and is called optical constant; τ is the turbidity of the solution; n_o is the refractive index of the solvent; λ is the wave length of the incident light; dn/dc is the refractive index increment of the solute. To find the molecular weight of a polymer the dn/dc values should be known. These dn/dc values are very much dependent upon concentration (5-7) and wave lenght [5,6.8] and is related in this way,

$$\Delta\bar{n}/c = a_1 + a_2 c \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where a_1 and a_2 are constants for a particular system; c is the concentration. The dn/dc for a small difference in concentration can be taken equal to $\Delta\bar{n}/c$. When it is ploted against concentration the intercept obtained in this way, is called specific refractive index increment and is denoted as γ, and V_2 is the specific volume of the polymer in

$$\nu_{\lambda_o}' - \nu_{\lambda_o}'' = v_2 [(n_2)_{\lambda_o}' - (n_2)_{\lambda_o}''] - [(n_o)_{\lambda_o}' - (n_o)_{\lambda_o}''] \quad \ldots\ldots\ldots\ldots (5)$$

solution and other have the same meanings. Specific refractive index increment is also related with the temperature by the equation given below,

$$d\gamma/dT = (\bar{n}_2 - \bar{n}_o)\, dv_2/dT + v_2 (d\bar{n}_2/dT - d\bar{n}_o/dT) .(6)$$

here T is the temperatur in absolute scale.

For this purpose we have considered a system of cellulose acetate in acetone, supplied by Kala Shah Kaku Rayon Ltd., Lahore. The dn/dc values of this system for a few fractions and for a wave length 546 nm. are given by Stein [9], for a wide range of concentration 1.0×10^{-5}

g/ml. to 6.0x10^{-2} g/ml) and for two wave lengths, 436 nm. and 546 nm. are given by us any where else [10], these values were determined at constant temperature 25^{o}.

The dn/dc values for three different wave lenghts and for three different concentrations having a very large difference so that one should be able to know the temperature dependence alongwith concentration are given here.

EXPERIMENTAL

Three different concentrations (0.06,0.60 and 1.61%) of cellulose acetate in acetone were prepared by dilution method, then for confirmation, the portion of them was dried at 60^{o} and concentration was again determined. For the measurements of △n/c Brice Phoenix Differential refractometer was used. This instrument was having mercurry are as a light source with two light filters of wave length 436 nm., and 546 nm. the third one of wave length 632 nm was inserted by ourselves.

The measurements were made at ten different temperatures by a difference of 5^{o} only and the temperature was changed from 10^{o} to 55^{o}. To keep the temperature constant a water bath thermostate was used, which was able to maintain the temperature up to ± 0.01^{o}. The water from that thermostate was circulated from the jacket of the measuring solution cell, so that we had a constant required temperature in the cell.

RESULTS AND IDSUSSION

The △n and △n/c for 0.06% and for all three wave lengths and for all the temperatures are given in the Table 1. Similarly for 0.60% and for 1.61% are given in the Table 2 and 3 respectively. This data is plotted in Figs. 1–3 for the

Table 1. △n and △n/c values for 0.06% concentration, taken at different temperatures and measured by using three wave lengths of light.

Wave lengths	436 nm		546 nm		632 nm	
Temp.°C	△nx10^4	△n/c (ml/g)	△nx10^5	△n/c (ml/g)	△nx10^5	△n/c (ml/g)
10	1.0056	0.1676	8.892	0.1482	7.950	0.1325
15	1.0188	0.1698	9.066	0.1511	7.986	0.1331
20	1.0362	0.1727	9.228	0.1538	8.142	0.1357
25	1.0494	0.1749	9.360	0.1560	8.286	0.1381
30	1.0656	0.1776	9.516	0.1586	8.436	0.1406
35	1.0812	0.1802	9.666	0.1611	8.580	0.1430
40	1.0962	0.1827	9.810	0.1635	8.724	0.1454
45	1.1112	0.1852	9.948	0.1658	8.850	0.1475
50	1.1256	0.1876	10.104	0.1684	9.003	0.1500
55	1.1406	0.1901	10.254	0.1709	9.150	0.1525

Table 2. Values of △n and △n/c for 0.60% concentration taken at different temperatures and measured by using three wave lenghts of light.

Wave lengths	436 nm		546 nm		632 nm	
Temp. °C	△n x 10^4	△n/c (ml/g)	△n x 10^5	△n/c (ml/g)	△n x 10^5	△n/c (ml/g)
10	7.098	0.1183	6.762	0.1127	6.390	0.1065
15	7.236	0.1206	6.876	0.1146	6.510	0.1085
20	7.368	0.1228	6.990	0.1165	6.630	0.1105
25	7.512	0.1252	7.116	0.1186	6.750	0.1125
30	7.650	0.1275	7.236	0.1206	6.636	0.1106
35	7.776	0.1296	7.350	0.1225	6.990	0.1165
40	7.902	0.1317	7.476	0.1246	7.098	0.1183
45	8.052	0.1342	7.590	0.1265	7.224	0.1204
50	8.178	0.1363	7.704	0.1284	7.338	0.1223
55	8.310	0.1385	7.830	0.1305	7.470	0.1245

Table 3. Values of △n and △n/c for 1.61% concentration, taken at different temperatures and measured by using three wave lengths of light.

Wave lengths	436 nm		546 nm		632 nm	
Temp. °C	△n x 10^4	△n/c (ml/g)	△n x 10^5	△n/c (ml/g)	△n x 10^5	△n/c (ml/g)
10	1.974665	0.1275	1.8679	0.1160	1.7642	0.1096
15	2.0020	0.1244	1.8953	0.1177	1.7939	0.1114
20	2.0253	0.1259	1.9192	0.1192	1.8137	0.1127
25	2.0537	0.1276	1.9441	0.1208	1.8378	0.1142

(continued. . . .)

(Table 3, continued. . . .)

30	2.0837	0.1294	1.9679	0.1222	1.8574	0.1154
35	2.1083	0.1310	1.9908	0.1237	1.8813	0.1169
40	2.1661	0.1345	2.0149	0.1252	1.9038	0.1183
45	2.1679	0.1347	2.0418	0.1268	1.9248	0.1196
50	2.1872	0.1359	2.0655	0.1285	1.9568	0.1225
55	2.2130	0.1375	2.0859	0.1296	1.9703	0.1224

respective concentration. The slopes are determined for all concentrations and for all wave lengths and are given in Table 4. The figs 1-3 show that the $\Delta n/c$ increases with temperature for all the concentrations and wave lengths. This type of systems are studied before [5,8] and the increase in $\Delta n/c$ is observed with temperature. The main reason is extent of solvation/solubility of polymers in solvents, as high molecular weight polymers have high values [11] of $\Delta n/c$.

We see that the slopes given in the Table 4 are different for every wave length, it may be due to difference in actual quantity of $\Delta n/c$. It can be concluded that the percentage change in $\Delta n/c$ with respect to temperature is constant for every wave length. The slopes also change with the change in concentration, the reason may be the same. The second reason may be the difference in concentration, which will result the difference in the expansion percentage of solute. The last reason will become clear

Table 4. Values of slopes of $\Delta n/c$ versus temperature for the three different concentration, and for three wave lenghts.

	$d(\Delta n/c) / dT \times 10^4$ ($ml\ g^{-1}\ deg^{-1}$)		
Wave lengths conc. %	436 nm.	546 nm.	632 nm.
0.06	5.10	4.91	6.32
0.60	4.52	4.01	3.85
1.61	3.28	2.70	3.125

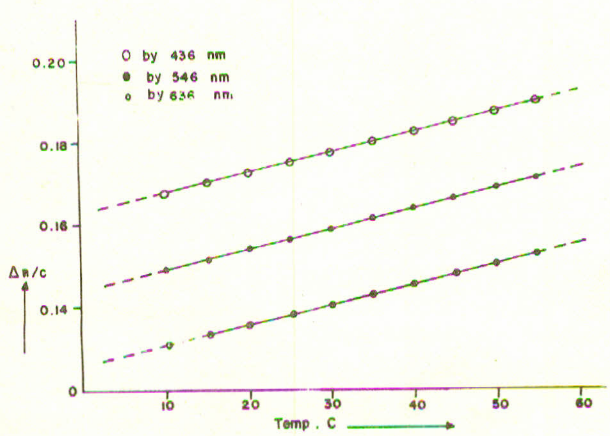

Fig. 1. $\Delta n/c$ versus temperature for 0.06% conc.

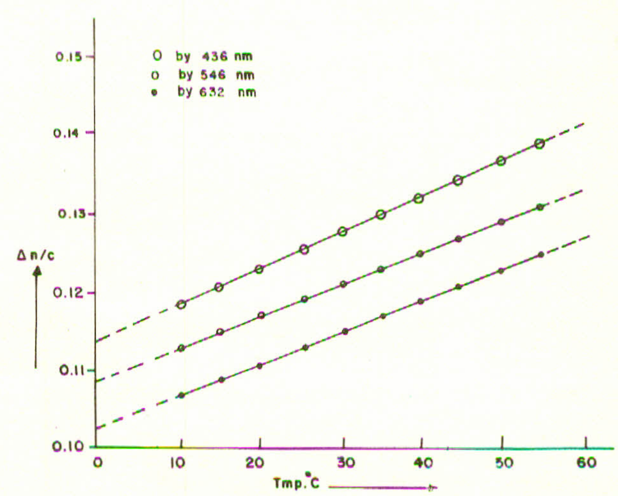

FIg. 2. $\Delta n/c$ versus temperature for conc. [illegible]60%.

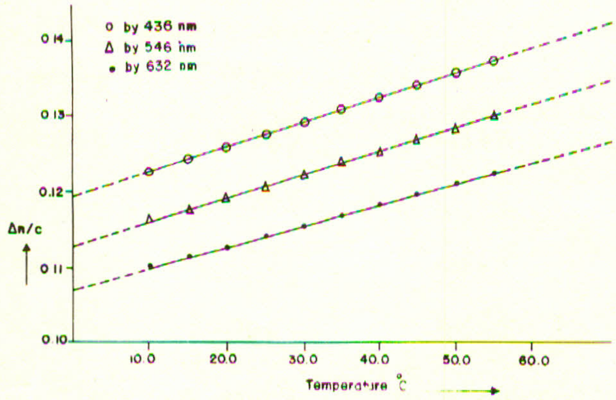

Fig. 3. Δn/c versus temperature for conc. 1.61%.

when the radius of gyration will be studied with respect to temperature. The maximum and minimum values of slopes are in the range of values already existing in the literature [5,8] for general cases.

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