

Electrical conductance of some cellulose derivatives

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SUMMARY:

The interrelation between the electrical conductance, σ and some chemically modified cellulose molecule produced through partial substitution of the hydroxyl groups by different groups namely, acetate, methoxyl, carboxymethyl and sodium carboxymethyl has been studied in the temperature ranges 283-333 K. The results show that σ of the examined samples change in the descending order: sodium carboxymethyl cellulose > carboxymethyl cellulose > methyl cellulose > cotton cellulose > cellulose acetate. The variable response of σ to the chemical modification and the physical changes of cellulose accompanying such modification has been discussed in terms of the molecular structure, chain flexibility and degree of polymerization of the examined samples.

INTRODUCTION

Although the problem concerning the electrical conductivity of polymeric materials and its dependence on several factors has been discussed previously (MURPHY 1929, HEARLE 1952, and ABDEL MOTELEB & NAOUM 1983), yet more work is still needed for a better understanding of such a problem. In a recent work (ABDEL MOTELEB and SHINOUDA 1989) a detailed study on the electrical conductivity of some cellulose materials of low moisture content and of different fine structure free of and contaminated with inorganic impurities of different nature has been carried out. The outcome of this work reveals that the mechanism by which the electric charge carriers migrate under the applied electric field at low moisture content of cellulose fibers differs from that if cellulose samples are of high moisture content. And that while the fine structure has little

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effect on such a property, the presence of even small amount of inorganic impurities has greater effect. Furthermore, in case of samples free of impurities, the ionization of the OH groups of cellulose molecule are responsible for electric current which is dependent on the degree of polymerization of the examined samples as well as the chain flexibility. The present work has been undertaken to study the interrelation between the partial substitution of the OH groups of cellulose on its electrical conductance.

EXPERIMENTAL

In the present work the materials used are the non-ionic macromolecules, namely cotton cellulose, cellulose acetate, methyl cellulose, carboxymethyl cellulose as well as the ionic polymer; sodium carboxymethyl cellulose. The ash contents of the non-ionic cellulose derivatives were determined and were found to be of undetectable amounts.

samples

cotton cellulose (sample I): obtained by purification of medicated cotton cellulose from inorganic contaminations by steeping in 5N HCl at room temperature for two hours as described before (ABDEL MOTELEB and SHINOUDA 1989). This sample has a DP= 2305 and x-ray indices 83%.

Cellulose acetate (sample II): of D.S.=2, DP=450 and x-ray crystallinity indices of 43%.

Methyl cellulose (sample III): of D.S.=2, of DP=450 and characterized by a diffuse x-ray diffraction pattern indicating a non crystalline material.

Samples II and III were from the same batches used before (AZIZ and SHINOUDA 1973).

Sodium carboxymethyl cellulose (sample IV): was kindly provided by Hercules manufactures, of D.S. = 0.7, of DP = 430 and of diffuse x-ray diffraction pattern.

Carboxymethyl cellulose (sample V): prepared from sample IV by treating 5 gms of this sample with a mixture of 100 parts of ethyl alcohol and 10 parts of nitric acid (PACAULT and BOUTTEMY 1950) and stirred mechanically for 30 min. Filtered and extracted in soxhlet with 70% methyl alcohol for two hours then rinsed with absolute alcohol and ether. Dried at 130 °C for 1 hour. This sample has a D.S. = 0.7 and of DP = 430.

Determination of the electrical conductance from dielectric loss measurements:

The dielectric loss, ϵ'' , was measured using NF dekameter type DK05 covering a frequency range from 0,03 to 100 Kcps. The

dielectric cell was kept dry during measurement as described before (ABDEL MOTELEB and NAOUM 1983). Measurements of loss were made at frequencies from 0.05 to 0.3 Kcps over the temperature range 283- 333 k.

The electrical conductance σ of the examined samples at any given temperature was calculated from the equation:

$$(\epsilon''f)_{f \rightarrow 0} / 1.8 \times 10^{12} \text{ ohm}^{-1} \text{ cm}^{-1}.$$

where $(\epsilon''f)_{f \rightarrow 0}$ was determined by plotting $\epsilon''f$ versus f and then extrapolated at zero frequency.

RESULTS AND DISCUSSION

The variation of the electrical conductance σ with temperature of the different samples examined is shown in Fig.1. A plot representing $\log \sigma$ versus $1/T$ is shown in Fig.2. From this figure the activation energy of conductance ΔE_{σ} was calculated and the results are cited in Table 1. This table also includes the values of σ of the samples examined at 293 k together with the degree of polymerization of such samples.

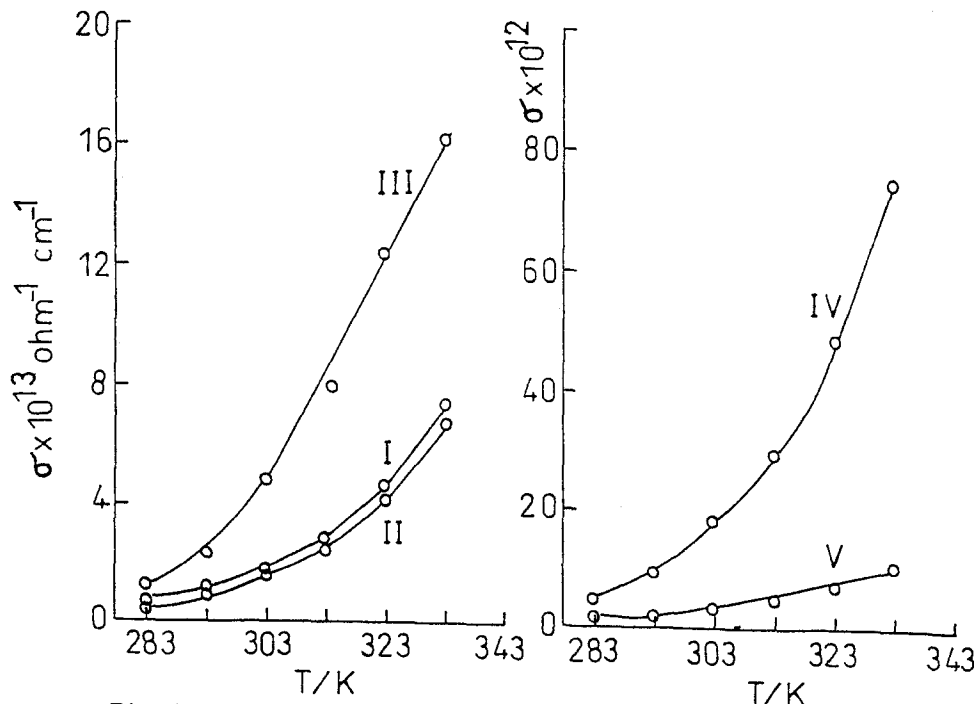


Fig.1: Variation with temperature of the electrical conductance of samples I, II, III, IV and V.

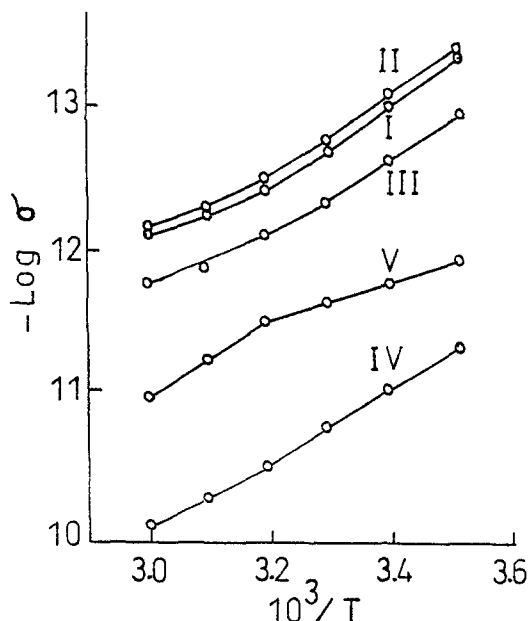


Fig.2: Variation of $\log \sigma$ with $1/T$ of samples I, II, III, IV and V.

TABLE (1)

Electrical conductance at 293 k together with the degree of polymerization, DP and the activation energy of conductance, ΔE_{σ}^* of some cellulose derivatives

Material	DP	$\sigma \times 10^{13}$ $\text{ohm}^{-1} \text{cm}^{-1}$	ΔE_{σ}^* K cal/mole	
			before T_r	after T_r
Cotton cellulose	2305	1.35	13.8	7.6
Cellulose acetate	450	1.15	15.2	9.7
Methyl cellulose	450	2.6	11.9	6.9
Carboxymethyl cellulose	430	16.6	6.9	11.5
Sodium carboxymethyl Cellulose	430	98.5	11.1	8.7

It is evident from these results that:

(i) at a given temperature the values of σ of the non-ionic polymers are in the order; cellulose acetate < cotton cellulose < methyl cellulose < carboxymethyl cellulose, (ii) the value of σ of the polyionic polymer sodium carboxymethyl cellulose is much higher compared with σ of the non-ionic derivatives examined, and (iii) the change of σ with temperature takes place exponentially with all the samples examined.

Before we discuss and analyse the present results of the

electrical conductivity and its variable response to chemical modification and temperature, it seems of important to consider the chemical and in turn the physical changes that take place during the partial substitution of the OH groups of cellulose molecule and the factors affecting the electrical conductivity of a given polymer. These can be summarized in the following: (i) while the partial substitution of the OH groups by non-ionic groups such as acetyl, methoxyl (samples II and III) would result in a decrease of the available OH groups accessible for ionization under electric field, the replacement of the OH by the more ionizable- CH_2COOH (sample V) results in an increase of the number of the electrical charge carriers, (ii) a pronounced increase in the ionic species is expected in case of the ionic polymer (sample IV), and (iii) some physical changes such as decrease in the DP., and a weakening of the degree of hydrogen bonding, as evidenced from the infrared spectra (SHINOUDA & HANNA 1977 and CROFTON et al. 1982). The latter may lead to an increase in the flexibility of the cellulose chain. However, in case of cellulose acetate, the polymer becomes more rigid due to the presence of the bulky acetate group and the formation of cross linking. In addition the electrical conductivity of polymers has been reported (ABDEL MOTELEB and SHINOUDA 1989) to depend mainly on the nature and magnitude of the current charge carriers, moisture content, the degree of polymerization, and the chain flexibility of the cellulose materials.

Based on the above explanation it seem probable that the difference between the values of σ for the samples examined II, III and V could be attributed most probably to the nature of the electrical charge carrier as well as the chain flexibility of cellulose; since these samples are of comparable DP, of low moisture contents and free of inorganic contaminations. Accordingly the lower values of the electrical conductance of cellulose acetate than that of cotton cellulose at any given temperature can be explained in view of the decreases of the OH groups due to partial substitution and the greater restriction of the migration of the charge carriers, where the presence of the bulk acetate groups leads to a steric constraints on the side group motion (CROFTON, et al. 1982) resulting in a reduction of the chain flexibility. On the other hand the higher values of σ of methyl cellulose compared with cellulose acetate could be attributed to the small size of the methyl group and the absence of cross linking. These would result in a higher flexibility and thus allow other units to be polarized and enhanced the mobility of the charge carriers responsible for the passage of the electric currents. And that the chain flexibility of cellulose molecules has an indirect but

pronounced effect on the mobility of the electrical charge carrier and in turn on the electrical conductance (ABDEL MOTELEB and SHINOUDA 1989) is justified in the present work from the result of the higher values of σ of the partial substituted methyl derivatives compared with that of the unsubstituted cellulose molecules, sample I.

Regarding carboxymethyl cellulose, the higher σ values of such a substance of the D.S.=0.7 than that of the unsubstituted cellulose as well as than those of samples II and III of comparable DP and of higher D.S. could be attributed to the more ionization of the carboxyl group compared with that of the hydroxyl, methyl and acetate groups at a given temperature and under the same electric field. On the other hand, the much higher values of σ of the sodium salt of carboxymethyl cellulose are due to the presence of the sodium ions, agreeing with the previous results (ABDEL MOTELEB and SHINOUDA 1989) which reveal that the contamination of even small amount of inorganic ions has a great effect on the electrical conductance of the cellulose substances.

The exponential variation of σ with temperature for all the samples examined of low moisture content and of different nature of charge carriers as shown in Fig. 1, may be explained most satisfactorily by activation jumps of the charge carriers from one region to another over the dielectric barriers created by the cellulose derivative. Increasing temperature, the carrier concentration does not change, but the mobility increases.

From Fig.2, it is clear that the change of $\log \sigma$ with $1/T$ for all samples examined (I \rightarrow V) exhibits a transition temperature, T_r , in the vicinity of 303 K confirming the previous results from other measurements (WAHBA et al. 1958, RAMIAH & GORING 1965, and SHINOUDA & HANNA 1975) that these samples exhibit a second order transition which is a property of hydrogen bonding.

The variation of ΔE_{σ}^* before and after T_r of the examined derivatives compared with the unsubstituted cellulose, could be explained if consideration is given to the previous conclusion (ABDEL MOTELEB and SHINOUDA 1989) that a relation does exist between the values of ΔE_{σ}^* and the cellulose chain flexibility.

Therefore, the high values of ΔE_{σ}^* before and after T_r in case of cellulose acetate compared with samples I, III and V could be attributed to the restriction of the migration of the charge carriers as a result of the steric hindrance of the bulky acetate group. And that the low values ΔE_{σ}^* in case of sample III compared with those of cotton cellulose reflect the increase in the chain flexibility which enhances the mobility

of ions.

In case of sample V, the pronounced change in ΔE_{O}^* before and after T_r and the higher value of ΔE_{O}^* after T_r compared with the other derivatives examined, could be explained in view of the following: (i) the change of the thermal coefficient of a certain characteristic property of a cellulose substance depends not only on the free OH groups and the hydrogen bonding between these groups, but also on the interchain spaces between cellulose chains (SHINOUDA and HANNA 1977) and (ii) the formation of a lactone ring in such a sample between -COOH and the unreacted OH group in the cellulose molecule upon drying (CHOWDHURY 1924). Based on these factors, it seems that the formation of the lactone ring provides more interchain spaces which expand with increasing temperature, and lead to a pronounced change in the observed ΔE_{O}^* of such a sample. This explanation is justified by the results of ΔE_{O}^* obtained in case of sodium carboxymethyl cellulose. These results when compared with those of sample V, show a reverse trend for the change of ΔE_{O}^* with temperature but similar trend when compared with those of samples I, II and III, indicating that the presence of sodium ions prevent the formation of the lactone ring and the values of ΔE_{O}^* of such sample reflect the ease of mobility of sodium ions as well as the other ions present in such sample.

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