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Research Note

Some preliminary studies on polyelectrolyte and rheological properties of sodium 2,3-dicarboxycellulose[a]

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Sodium 2,3-dicarboxycellulose (NaDCC) was synthesised, and its polyelectrolyte behaviour was compared to a commercial sample of sodium carboxymethyl cellulose (NaCMC), and to sodium alginate data from literature. NaDCC showed typical polyelectrolyte properties, such as viscosity and flocculation of multivalent salts. In spite of very low viscosity of aqueous NaDCC solution due to very low molecular weight, the flocculation of $Al_2(SO_4)_3$ from aqueous solutions using NaDCC was quite comparable to NaCMC. Preliminary studies on the rheology of NaDCC were also carried out. The rheological properties of NaDCC were in contrast to that of NaCMC reported in literature. This was because of the vast difference in their molecular weights, which resulted in their rheograms being investigated in very different shear rate regions. The NaDCC solutions showed slight shear thickening behaviour.

INTRODUCTION

Cellulose derivatives constitute a very important segment of the world market for water soluble polymers. Their industrial applications cover a very wide range due to a variety of functional characteristics. Cellulose derivatives are generally considered to be biocompatible, biodegradable and non-toxic, and are derived from cellulose, which is the most abundant renewable resource produced by nature from a variety of plant life. It is estimated that 100 billion tonnes of cellulose in the form of renewable vegetation is produced every year on this planet (Fyfe *et al.*, 1983). Amongst cellulose derivatives, sodium carboxymethyl cellulose occupies perhaps the highest position in terms of industrial usage. It is an anionic water-soluble polyelectrolyte having a broad range of applications in the food, pharmaceutical, cosmetic, laundry, textile, paper, petroleum, detergent and many other industries. It is, therefore, of great interest to search for new anionic derivatives of cellulose, which may out perform sodium carboxymethylcellulose (NaCMC) in properties and economics. Salts of 2,3-carboxycellulose have been prepared and some of their properties have been reported (Maekawa & Kosijima, 1984). However, their rheological behaviour has not been much investigated. As part of our ongoing research in the area of oxidized cellulose derivatives (Varma & Jamdade, 1985; Varma *et al.*, 1985, 1991) we felt it would be of interest to synthesise water-soluble sodium 2,3-dicarboxycellulose and investigate its rheological properties. The structure of this polymer is such that it does not have any glucopyranose units which constitute the cellulose chain. Therefore, this polymer would not have the same degree of chain stiffness as sodium carboxymethylcellulose in which all the glucopyranose monomer units are intact. Further, this polymer would have two carboxylate functional groups per glucose monomer unit in fixed C_2 and C_3 positions, while NaCMC has the carboxylate group in C_6 position.

In this investigation, a series of sodium dicarboxy celluloses (NaDCC) were prepared wherein the degrees of oxidation of cellulose were 12, 30, 60, 80 and 98%,

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based on glucopyranose units. Solubility studies indicated that only 98% NaDCC was water-soluble. Hence it was selected for investigating its polyelectrolyte and rheological properties. Data on these aspects are presented in this paper, and the results compared with NaCMC.

EXPERIMENTAL

Synthesis of NaDCC

Stoichiometric quantities of sodium metaperiodate and cellulose powder were reacted in the dark at 55°C for 6 h to give the corresponding cellulose dialdehyde (Nevell & Whistler, 1963). The aldehydes were further oxidized with excess sodium chlorite and acetic acid at 20°C for 7h (Varma & Jamdade, 1985). After the reaction, N_2 gas was bubbled to remove dissolved chlorine dioxide gas. Recovery of the product was carried out in the usual way, as described in the literature (Nevell & Whistler, 1963). The reaction scheme is shown in Fig. 1. The excess salt, if any, was removed by repeatedly dissolving the NaDCC in distilled water and precipitating in three times its volume of ethanol.

Sodium analysis of 98% NaDCC

Solutions of 98% NaDCC (concentration range 3–5 ppm) were tested for Na by use of Atomic Absorption Spectrophotometer model Z-8000 (Hitachi). Operating conditions of analysis were: slit 0·4 nm, wavelength 589·6 nm and lamp current 7·5 mA. Complete agreement between the experimental and theoretical value (i.e. 19·65% sodium content) was obtained.

Viscosity measurements

An ubbelohde viscometer immersed in a constant temperature water bath maintained at 25°C was used for all viscosity measurements. NaCMC and NaDCC concentrations in the range 1×10^{-2}%–1·00% with and without added sodium chloride were studied. Flow time measurements were made in triplicate and the average value was taken for calculations. For one study, a Brookfield Viscometer model DV-I with digital readout was used.

Rheological study

A Ferranti–Shirley cone-plate viscometer was used for aqueous solutions of NaDCC at 200–800 rpm.

Procedure for flocculation

10 ml of 1×10^{-2} M NaDCC was added to a beaker containing 40 ml distilled water. In another beaker 10 ml of 1 M $Al_2(SO_4)_3$ was diluted with 40 ml distilled water and added dropwise to the polymer solution under vigorous stirring for 10 min, and then left standing for 24 h. The flocculated materials were filtered using Whatman filter paper No. 1, and dried at 50°C under vacuum and weighed. In a similar manner, flocculation of more dilute $Al_2(SO_4)_3$ solutions, namely 1×10^{-2}, 5×10^{-2} and 5×10^{-3} M and NaCMC solutions were carried out. The results are reported in Table 1.

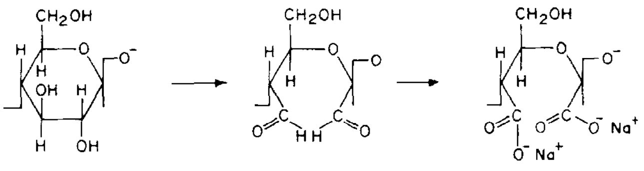

Fig. 1. Reaction scheme for synthesis of sodium 2,3-dicarboxycellulose (NaDCC).

Table 1. Flocculation data on the treatment of various concentrations of $Al_2(SO_4)_3$ dissolved in water with 1×10^{-3} mol/l aqueous solutions of NaCMC and NaDCC at room temperature

$[Al_2(SO_4)_3]$ (mol/l)	Wt. of flocculant using NaCMC (g)	Wt. of flocculant using NaDCC (g)
5×10^{-3}	3·44	2·45
1×10^{-2}	5·30	2·78
5×10^{-2}	7·21	2·97
1×10^{-1}	7·65	3·20

Total volume of $Al_2(SO_4)_3$ solution and polymer solution was kept constant at 100 ml.

RESULTS AND DISCUSSION

Figure 2 shows that for an aqueous solution of NaDCC, the reduced viscosity increases continuously with a decrease in concentration when there is no salt added. This is the typical behaviour of a polyelectrolyte. With added salt also, the general trend is in agreement with reported results for NaCMC, sodium pectinate etc. (Fujita & Homma, 1955; Pals & Hermans, 1948). The general effect of addition of a simple salt is to depress the viscosity of the polyelectrolyte solution over the entire range of concentrations (Mandel, 1988). Due to severe chain degradation during the course of the oxidation reaction used in synthesising NaDCC, the reduced viscosities observed were very low. Comparing the reduced viscosity data of NaDCC presented in Fig. 2 with similar data on NaCMC of D.P. 417 reported by Fujita and Homma (1955), we find that our values of reduced viscosities are lower by more than an order of magnitude under identical conditions (in the range of 30–50 times lower). Assuming similar values of K and a in the relationship $\eta = KM^a$, the D.P. of NaDCC may be 8–14. In order to check that even in industrial appli-

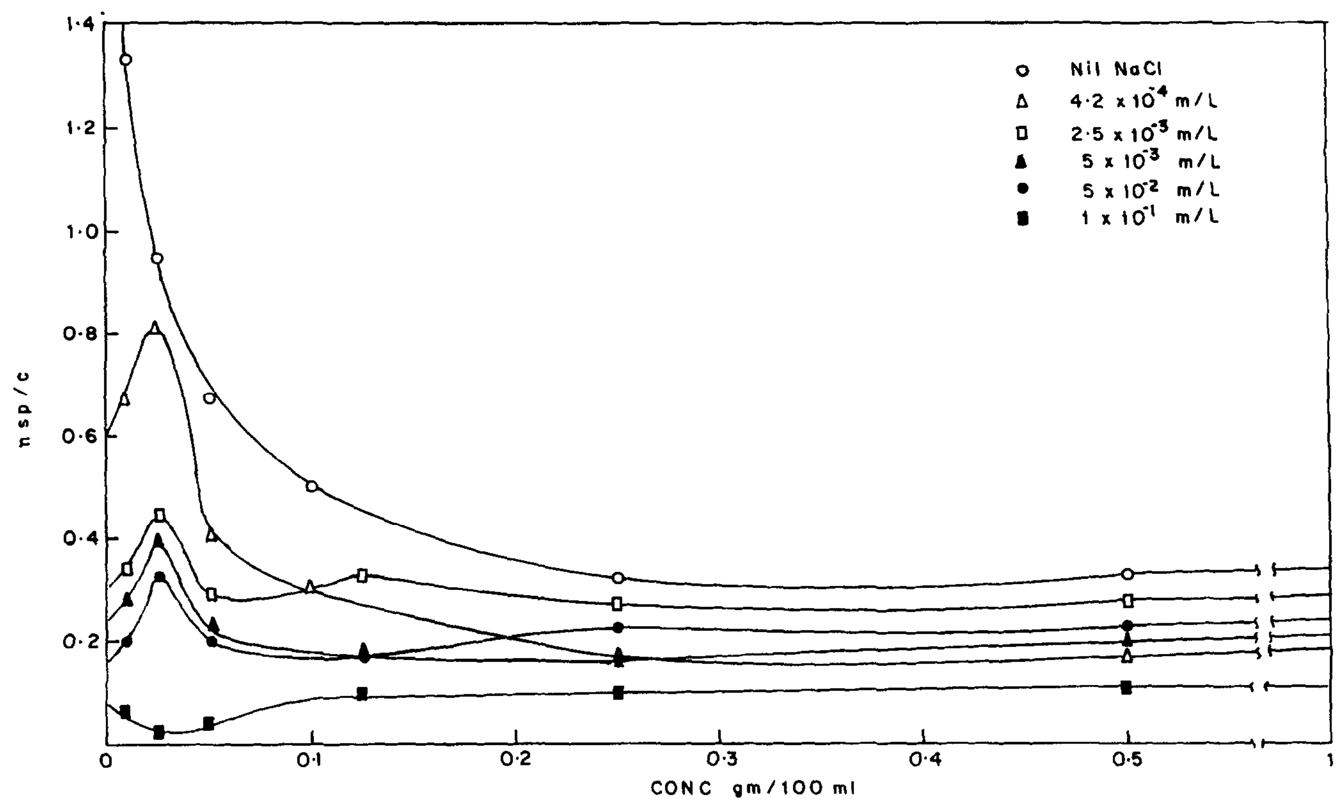

Fig. 2. Reduced viscosity (η_{sp}/c) vs concentration (g/100 ml) of NaDCC in aqueous solution with and without added NaCl: ○, without added NaCl; △, 4·2 × 10^{-4} mol/l NaCl added; □, 2·5 × 10^{-3} mol/l NaCl added, ▲, with 5 × 10^{-3} mol/l NaCl added; ●, 5 × 10^{-2} mol/l NaCl added; ■, 1 × 10^{-1} mol/l NaCl added.

cations NaDCC behaves like a polyelectrolyte, in spite of very low molecular weight, we studied the flocculation of multivalent salts such as $Al_2(SO_4)_3$ using our low molecular weight NaDCC (viscosity 1·1 centipoise (cP)), and a commercial higher molecular weight NaCMC (viscosity 12 cP). The results are presented in Table 1. Apparently, the presence of two carboxylate groups close together on the NaDCC chain plays a role in flocculation.

Narayan and Ramasubramanian (1982) studied the rheological behaviour of aqueous solutions of NaCMC and sodium alginate in the concentration range of 3·0–3·5%. In both cases, they observed a drop in viscosity with increasing shear rate. This is in contrast to our observation (Fig. 3) of increasing viscosity with shear rate. However, in our case the maximum viscosity of 3% NaDCC was only 1·94 cP, and a very high shear rate (13,500 s^{-1}) was used. In the case of NaDCC for a 3·5% aqueous solution at 25°C, the viscosity was 3911 cP at a shear rate of 7·05 s^{-1} dropping to 272 cP at a shear rate of 1142 s^{-1} (Narayan & Ramasubramanian, 1982). Therefore, our observations pertain to a much higher shear rate region, and the two systems are not strictly comparable. We are now attempting to synthesise high molecular weight NaDCC (using noble metal catalyst systems), so that its solution properties can be compared with NaCMC. For the moment, however, the preliminary observations on the shear thickening behaviour of NaDCC seem to be an exciting property.

A rheogram of shear stress vs shear rate for a 3% aqueous NaDCC solution is presented in Fig. 4. The shear stress is increased from 32·79 to 262·31 dynes/cm^2 and the corresponding shear rate goes up from 3400 to 13,500 s^{-1}. Now, as the shear stress value is seen to decrease continuously, the shear rate is also seen to decrease, but has a value lower than what was observed earlier with increasing shear stress. For example, at a shear stress of 76·51 dynes/cm^2, the shear rate was 5075 when the reading was taken with continuously increasing shear stress, but was only 4230 when the reading was taken with continuously decreasing shear stress. The hysteris loop is shown in Fig. 4. This behaviour, again, was the reverse of what has been reported for NaCMC (deButts *et al.*, 1957). It is well known that most shear-thickening polymers contain functional groups which are capable of associating, both intramolecularly and intermolecularly, through ionic or dipolar interactions, H-bonding, insolubility in the medium, etc. There are reports of quantitative theories for explaining the phenomenon of shear thickening in polymers (Ballard *et al.*, 1988).

In conclusion, it is clear that even low molecular weight NaDCC shows polyelectrolyte behaviour, and also some interesting rheological properties. This poly-

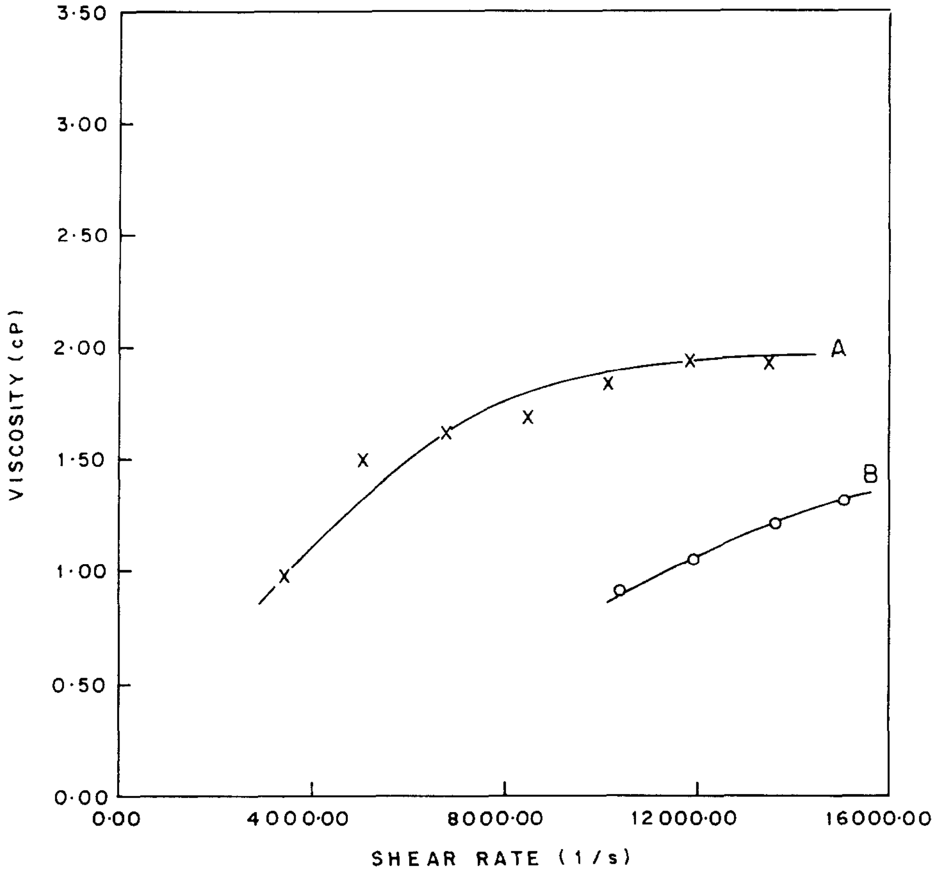

Fig. 3. Brookfield viscosity (cP) vs shear rate (s) of NaDCC in aqueous solution: (A) 3%: and (B) 1·5%.

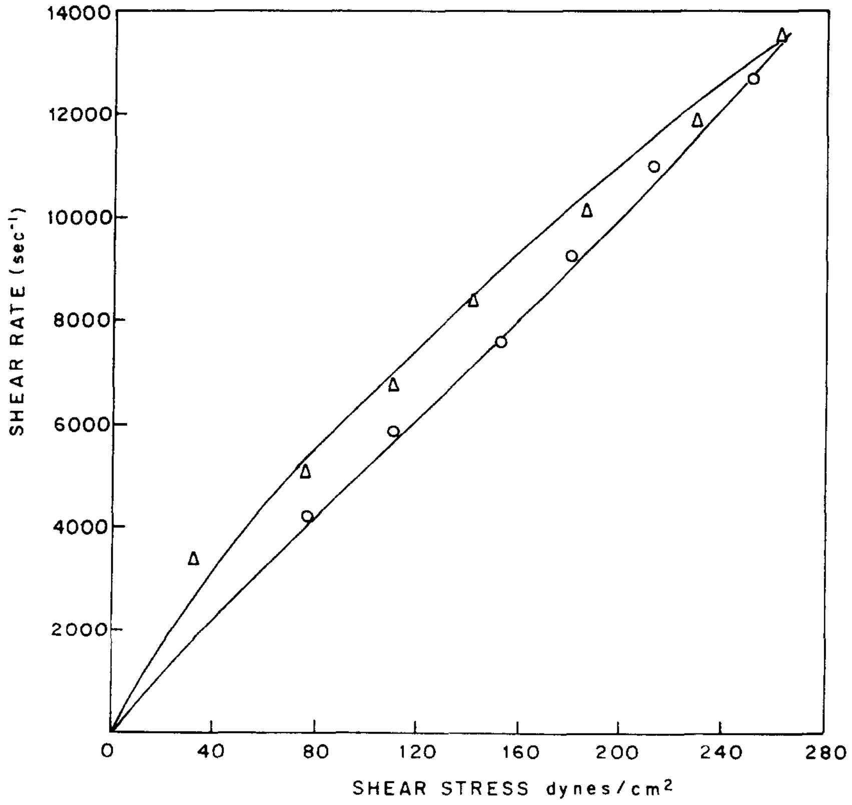

Fig. 4. Rheogram of NaDCC solution.

mer, if synthesised with higher molecular weights, may have interesting rheological properties for industrial applications.

REFERENCES

Ballard, M.J., Buscall, R. & Waite, F.A. (1988). *Polymer*, **29,** 1287–93.

deButts, E.H., Hudy, J.A. & Elliott, J.H. (1957). *Ind. Eng. Chem.*, **49**(1), 94–8.

Fujita, H. & Homma, T. (1955). *J. Polym. Sci.*, **XV,** 277–95.

Fyfe, C.A., Dudley, R.L., Stephenson, P.J., Deslandes, Y., Hamer, G.K. & Marchessault, R.H. (1983). *J. Macromol. Sci., Rev. Macromol. Chem. & Phys.*, **C23**(2), 187–216.

Maekawa, E. & Kosijima, T. (1984). *J. Appl. Polym. Sci.*, **29,** 2289–97.

Mandel, M. (1988). In *Encycl. Polym. Sci. & Eng.*, Vol. 11, 739–829.

Narayan, K.S. & Ramasubramanian, V. (1982). *Ind. J. Technol.*, **20,** 333–8.

Nevell, T.P. & Whistler, R.L. eds (1963). *Methods in Carbohydrate Chemistry*, Vol. III. Academic Press, New York, p. 164.

Pals, D.T.F. & Hermans, J.J. (1948). *J. Polym. Sci.*, **3**(6), 897–8.

Varma, A.J., Chavan, V.B., Rajmohanan, P.R. & Ganapathy, S. (1991). All India Conf. at BHU, Varanasi, 7 Feb.

Varma, A.J. & Jamdade, Y.K. (1985). *Carbohydr. Polym.*, **5,** 309–16.

Varma, A.J., Jamdade, Y.K. & Nadkarni, V.M. (1985). *Polym. Degrad. and Stab.*, **13,** 91–8.