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Mesophase formation and intrinsic viscosity for some low-molecular-weight cellulose acetate samples

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The intrinsic viscosity $[\eta]$ of cellulose acetate (CA) has been determined in two solvents: acetic acid (AA) and *N,N*-dimethylacetamide (DMAC). The samples of this cellulose derivative have a rather weak mean molecular weight \overline{MW} , with a mean degree of polymerization \overline{DP} ranging from 213 to 47 and the same origin. We use the theory of Yamakawa for a worm-like chain to obtain the hydrodynamic diameter D and the persistence length q for these samples of CA, and the Mark-Houwink equation to estimate the parameters K and α . These results were compared with the same parameters obtained with previous experimental published results for CA with a high MW. The measurements were also carried out at different temperatures; the intrinsic-viscosity temperature dependence is discussed. The D and q values calculated for the low-MW range allow estimation of the critical concentrations C^* for the solutions, which are compared with experimental results.

1. Introduction

There have been a number of studies (see e.g. [1, 2]) of cellulose acetate, which is an industrially interesting product.

Yamakawa's model for a worm-like chain [3] has been used in previous papers [4, 5] to estimate the persistence length and the hydrodynamic diameter of polymer chains through intrinsic-viscosity measurements on polymer solutions.

The present paper is a contribution to the investigation of cellulose derivatives through similar experiments on cellulose acetate (CA) fractions of low molecular weight.

2. Experimental

The characteristics of the cellulose acetate samples used are given in table 1.

The solvents used were acetic acid (AA) and dimethylacetamide (DMAC), obtained from Aldrich, (99 + % Gold Mark); they were used without further purification.

Viscosimetric measurements were performed using an Ubbelohde viscosimeter with a capillary tube of 0.58 mm diameter for all solutions, except for the measurements on solutions of CA in AA for temperatures up to 50°C, where the capillary tube used was of 0.36 mm diameter. The viscosimeter was maintained at constant temperature in a thermostatic bath ($\pm 0.1^\circ\text{C}$). The concentrations of CA in the two solvents ranged from 0.9×10^{-3} to 12.0×10^{-3} g ml⁻¹. The intrinsic viscosity as a function of MW and temperature are given for each system in tables 2 and 3.

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Table 1. Characteristics of the CA samples used in this work.

| Sample number | \overline{DP}^\dagger | DS | \overline{MW} | Percentage acetic acid † | Unit MW | Percentage acetyl |
|---------------|-------------------------|------|-----------------|-----------------------------------|---------|-------------------|
| 1 | 213.0 | 2.51 | 56 961 | 56.27 | 267.42 | 40.34 |
| 2 | 189.5 | 2.31 | 49 084 | 53.50 | 259.82 | 38.35 |
| 3 | 137.5 | 2.46 | 36 481 | 55.57 | 265.32 | 39.83 |
| 4 | 110.0 | 2.49 | 29 324 | 56.07 | 266.58 | 40.19 |
| 5 | 93.5 | 2.45 | 24 768 | 55.47 | 264.90 | 39.76 |
| 6 | 89.0 | 2.49 | 23 726 | 55.97 | 266.58 | 40.12 |
| 7 | 75.5 | 2.48 | 20 095 | 55.87 | 266.16 | 40.05 |
| 8 | 73.0 | 2.48 | 19 430 | 55.83 | 266.16 | 40.02 |
| 9 | 47.0 | 2.45 | 12 450 | 55.48 | 264.90 | 39.77 |

† Measurements made by Rhodia Industry.

Table 2. Intrinsic viscosity as a function of molecular weight for DMAC/CA and AA/CA at room temperature ($t \approx 23^\circ\text{C}$).

| DMAC/CA $[\eta]/\text{cm}^3 \text{g}^{-1}$ | AA/CA $[\eta]/\text{cm}^3 \text{g}^{-1}$ | \overline{MW} |
|---|---|-----------------|
| 158 | 179 | 56 961 |
| 141 | 153 | 49 084 |
| 113 | 122 | 36 481 |
| 78 | 85 | 29 324 |
| 66 | 74 | 24 768 |
| 52 | 65 | 23 726 |
| 45 | 53 | 20 095 |
| 27 | 33 | 12 450 |

Table 3. Intrinsic viscosity as a function of temperature for two different molecular weights and for both systems DMAC/CA and AA/CA.

| $t/^\circ\text{C}$ | | $[\eta]/\text{cm}^3 \text{g}^{-1}$ | | \overline{MW} |
|--------------------|-------|------------------------------------|-------|-----------------|
| DMAC/CA | AA/CA | DMAC/CA | AA/CA | |
| 30 | 30 | 129 | 147 | 56 961 |
| — | 40 | — | 133 | |
| 50 | 50 | 106 | 124 | |
| — | 60 | — | 122 | |
| — | 70 | — | 112 | |
| — | 30 | — | 73 | 29 324 |
| 40 | 39 | 64 | 67 | |
| 50 | 50 | 62 | 64 | |

The concentration at which the birefringence appears will be termed the critical concentration C^* ; it was evaluated using an Olympus polarizing microscope. The temperature dependence was studied using a Mettler hot stage. The solutions were placed between glass slides and the intensity of light transmitted by the anisotropic sample, between crossed polarizers, was recorded by a photomultiplier connected to a graphic plotter. Plots of C^* versus degree of polymerization DP at room temperature ($t \approx 23^\circ\text{C}$) for solutions of CA in AA and DMAC are presented in figure 1, and the values are given in table 4. Figure 2 shows C^* as a function of temperature for two

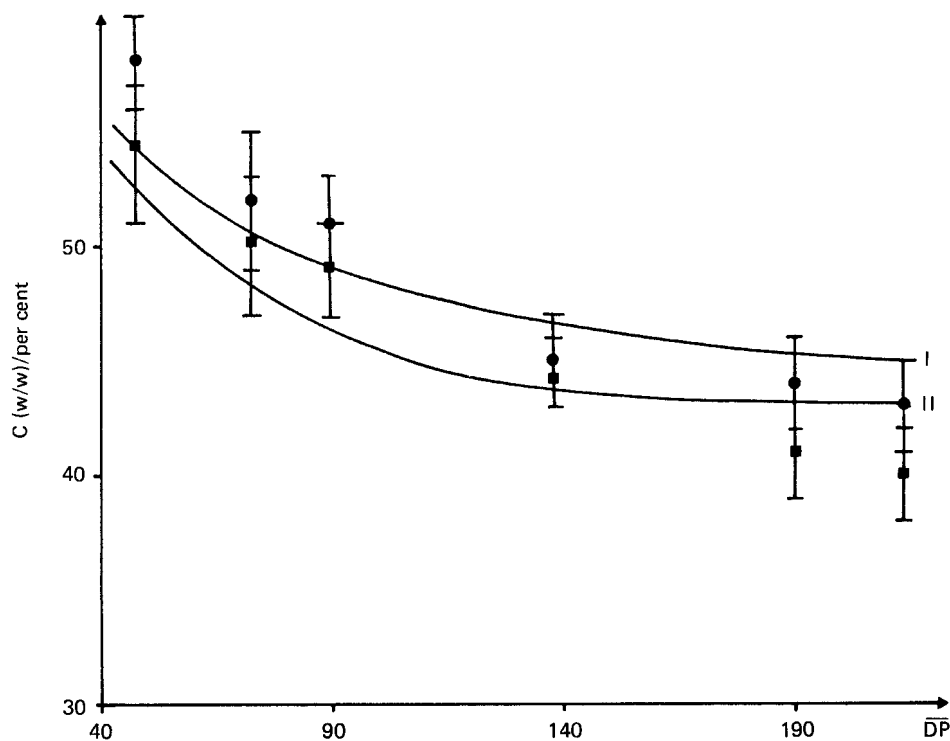


Figure 1. Critical concentration versus mean degree of polymerization at room temperature: ●, AA/CA; ■, DMAC/CA (experimental points); curve I, theoretical prediction for AA/CA; curve II, theoretical prediction for DMAC/CA.

Table 4. Mean degree of polymerization \overline{DP} as a function of critical concentration for room temperature ($t \approx 23^\circ\text{C}$).

| \overline{DP} | DMAC/CA | AA/CA |
|-----------------|--------------------|--------------------|
| | C (w/w)/per cent | C (w/w)/per cent |
| 213.0 | 40.0 | 43.5 |
| 189.5 | 41.0 | 44.0 |
| 137.5 | 44.4 | 45.0 |
| 89.0 | 48.6 | 51.0 |
| 73.0 | 50.5 | 52.5 |
| 47.0 | 54.2 | 58.5 |

different molecular weights ($MW = 19430$ and 12450) of cellulose acetate in AA solution.

3. Results and discussion

Figures 3 and 4 show the $\log [\eta]$ versus $\log MW$ at room temperature ($t \approx 23^\circ\text{C}$) for two different solvents: DMAC and AA. Two important effects should be noted.

For a given solvent, a change in the molecular-weight range from $12450 < MW_1 < 56961$ to $61000 < MW_2 < 185000$ [6] for DMAC and to $34000 < MW_2 < 104000$ [7] for AA leads to a change in the slope of the curve of $\log [\eta]$ versus $\log MW$ (figure 3) and correspondingly the values of α and K from the Mark-Houwink

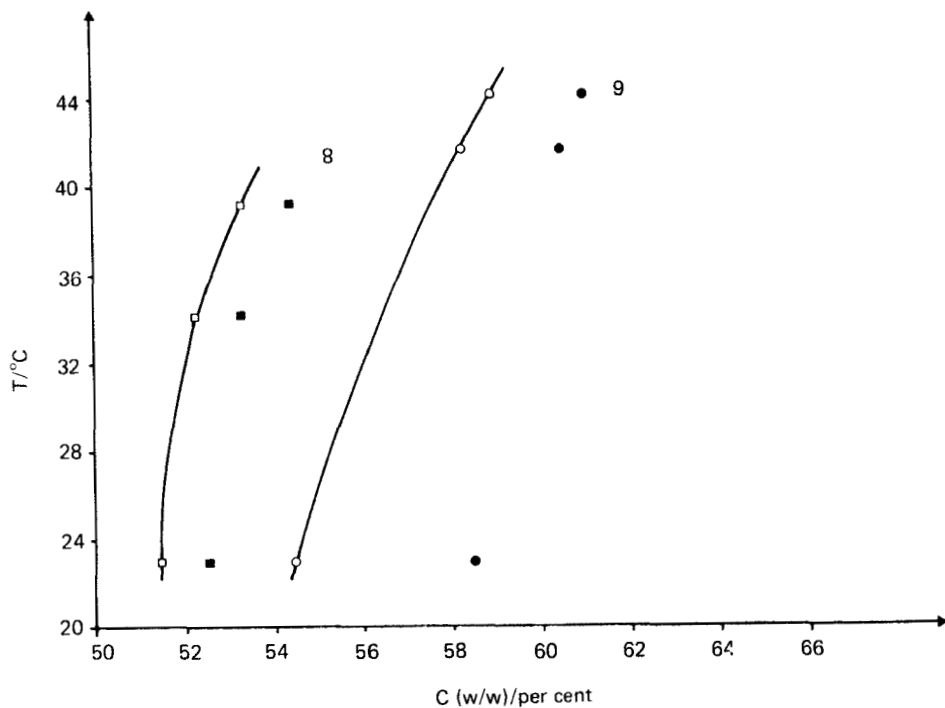


Figure 2. Temperature versus critical concentration for the system AA/CA: ■, experimental points for sample number 8; ●, experimental points for sample number 9; □, theoretical points for sample number 8; ○, theoretical points for sample number 9.

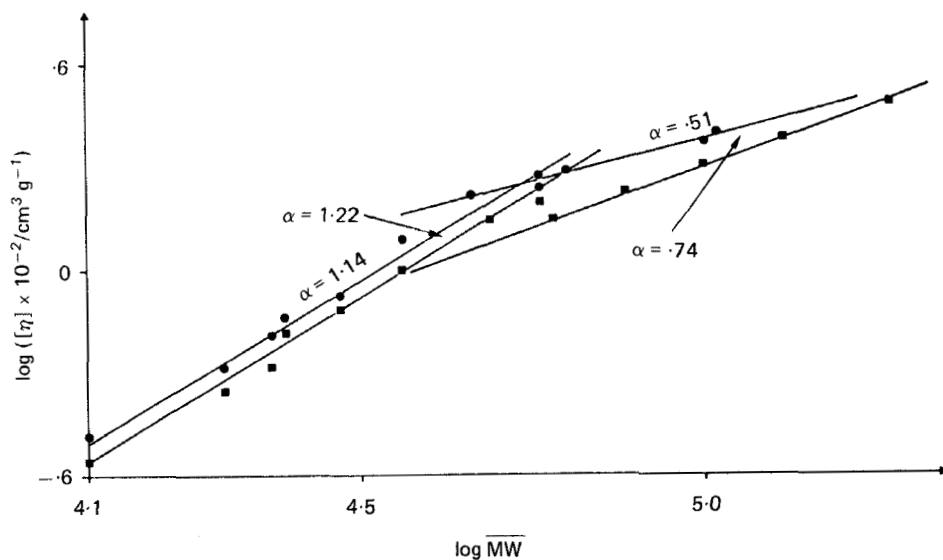


Figure 3. Intrinsic viscosity versus molecular weight at room temperature ($t \approx 23^\circ\text{C}$): ●, AA/CA; ■, DMAC/CA.

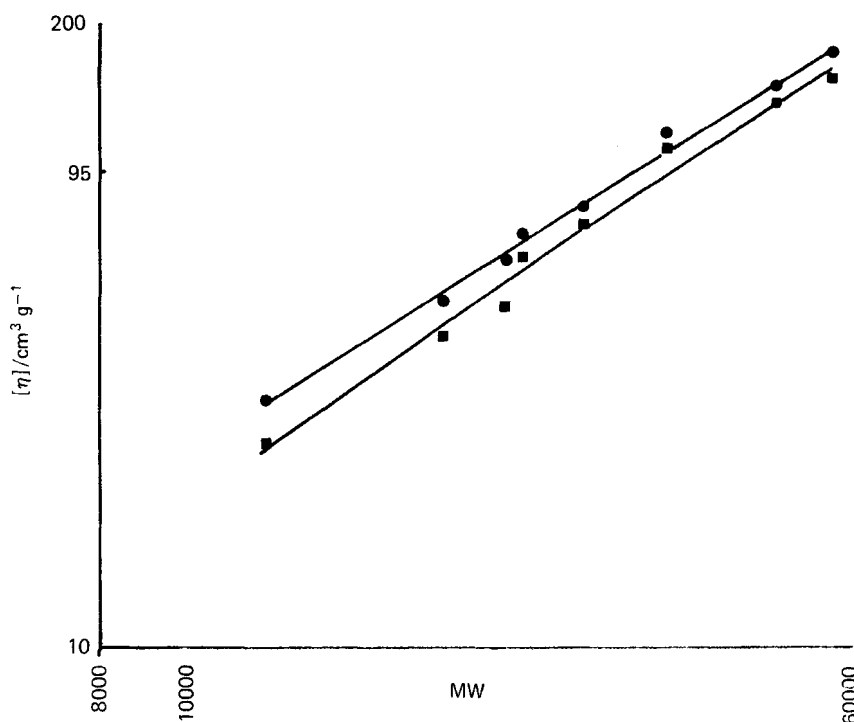


Figure 4. Intrinsic viscosity versus molecular weight at room temperature ($t \approx 23^\circ\text{C}$) (Yamakawa's model): ●, AA/CA; ■, DMAC/CA.

Table 5. Parameters α and K from Mark-Houwink equation and D and q from Yamakawa's theory as functions of molecular weight for DMAC/CA and AA/CA at room temperature ($t \approx 23^\circ$).

| | DMAC/CA | | AA/CA | |
|-----------------|---------|------|-------|------|
| | MW1 | MW2† | MW1 | MW2‡ |
| α | 1.22 | 0.74 | 1.14 | 0.51 |
| $K \times 10^6$ | 2.69 | 395 | 6.78 | 6840 |
| $D/\text{\AA}$ | 5.6 | 13 | 9.7 | 18.0 |
| $q/\text{\AA}$ | 139.9 | 66 | 130.3 | 89.1 |

† Calculated using values from [6].

‡ Calculated using values from [7].

equation [8] are rather different (table 5). The variations of q and D obtained from Yamakawa's model as explained previously [4] are also observed for the two different ranges of molecular weights and for both solvents (table 5); the theoretical plots (from Yamakawa's model) are shown for the low-molecular-weight range in figure 4. The parameters α and q are greater for the MW1 range than for the MW2 one, so that the chains of low molecular weight may be more rigid.

The other effect that can be seen from figure 3 is the importance of the solvent; if we consider both systems AA/CA and DMAC/CA, we observe that for the same temperature and same MW the $[\eta]$ values are slightly higher for the first system. However, the values obtained for q and D for the MW1 range show a weak effect of

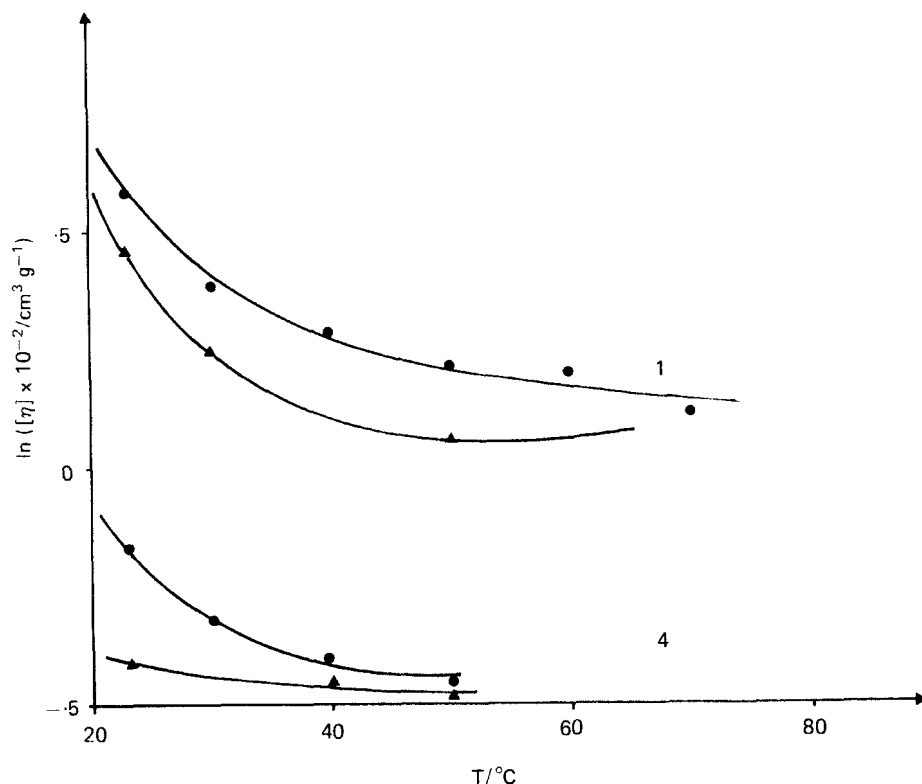


Figure 5. Intrinsic viscosity versus temperature for AA/CA (●) and DMAC/CA (▲); samples one and four.

Table 6. q and D for AA/CA system as functions of temperature based on values obtained for samples one and four.

| $t/^\circ\text{C}$ | $q/\text{\AA}$ | $D/\text{\AA}$ |
|--------------------|----------------|----------------|
| 23 | 127 (130.3) | 8.9 (9.7) |
| 30 | 101.6 | 8.1 |
| 40 | 91.3 | 7.5 |
| 50 | 82.0 | 7.9 |

the solvent on the persistence length, $q_{\text{DMAC}} > q_{\text{AA}}$ (table 5), but with $D_{\text{AA}} < D_{\text{DMAC}}$ the values of the hydrodynamic diameters indicate us that there may be a specific interaction between the solvents and the cellulosic backbone.

Figure 5 shows the variation of $[\eta]$ with temperature for DMAC and AA for two different molecular weights ($\text{MW} = 56\,961$ and $29\,324$). For a given $[\eta]$ is a decreasing function of temperature for both molecular weights. This leads to a decrease in the D and q values as functions of temperature (see table 6).

The existence of plateau regions, which are related generally to helix/coil conformational transitions—as has been shown in the case of cellulose tricarbaniolate [9, 10]—is still under investigation for CA samples.

From figure 1 we can see that for a given solvent, when the DP increases, C^* decreases, which is qualitatively in agreement with theoretical predictions [11–13].

The concentrations at which birefringence appears are very narrow for both systems.

From the phase diagrams in figure 2 we can see that the transition temperature from the biphasic (anisotropic + isotropic) to the isotropic phase increases significantly with the concentration of the polymer—and this is an effect that is observed for both molecular weights under consideration (MW = 19 430 and 12 450). We can compare these results with Flory's theory through the use of $C^*(v/v) = 8/x$, with x equal to the reduced Kuhn segment $2q/D$ in the case of a semirigid chain [14]. This leads to $C^*(w/w) = 36.51$ per cent for AA/CA and $C^*(w/w) = 23.68$ per cent for DMAC/CA, but we cannot take into account the effect of the degree of polymerization.

On figures 1 and 2 we have also plotted the theoretical curves obtained through the use of the elastic worm-like chain model for the nematic/isotropic pseudo-transition [15]. The orientational interaction parameter values were taken to be $u = 0.48 \text{ kcal mol}^{-1}$ for the AA/CA system and $u = 0.54 \text{ kcal mol}^{-1}$ for the DMAC/CA system. We can see rather good agreement with experimental values for this model, which takes into account the semirigidity of the chains and the existence of orientational interaction between polymer segments ($C_{\text{exp}}^* - C_{\text{th}}^* < 4$ per cent).

4. Conclusion

We have obtained an estimate of the rigidity of CA samples of rather low molecular weight through intrinsic-viscosity measurements in AA and DMAC. The q values were obtained from Yamakawa's theory for worm-like chains. A comparison with previous works on CA samples of higher molecular weight leads us to think that the lower-molecular-weight samples are more rigid. The values of the Mark-Houwink plots give the same conclusion.

We have also performed measurements of the critical concentration C^* of AA/CA and DMAC/CA systems. We have rather good agreement with the theoretical predictions given by an elastic worm-like chain model for the nematic/isotropic pseudo-transition. The results presented are not conclusive with regard to the existence of a plateau region as noted previously for cellulose tricarbonylate solutions; this needs further investigation.

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