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Liquid crystalline solutions of cellulose acetate in phosphoric acid

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Abstract

The influence has been studied of both the acid strength of phosphoric acid and the degree of substitution of cellulose acetate on the formation of an anisotropic phase. The solvent composition is expressed as a P_2O_5 concentration. It was found that the clearing temperature increases strongly with decreasing amount of water in the solvent.

The influence of the degree of substitution (DS) was studied on a series of samples with a DS ranging from 0.23 to 2.89. It was found that over the entire range good solubility occurred in anhydrous phosphoric acid. The DS hardly affected the clearing temperature in the process of dissolving a constant number density of polymer chains. However, the birefringence of the solution was strongly influenced by the DS, due to the intrinsic birefringence of the polymer chains. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cellulose derivatives; Phosphoric acid; Liquid crystalline solutions

1. Introduction

1.1. Liquid crystalline solutions of cellulose and cellulose derivatives

Cellulose and its derivatives have been the subject of extensive investigations. The first publication on a cellulose-based liquid crystalline solution was by Werbowyj and Gray [1] and dealt with hydroxypropyl cellulose in water although before this publication a DuPont patent application on lyotropic systems of various cellulose derivatives in a great variety of solvents had been filed by Panar and Willcox [2]. Since then many more systems, forming anisotropic solutions have been found. Gray [3] has summarised the conditions for mesophase formation of cellulose-based systems: mesophase formation is promoted by making use of strongly polar or acidic solvents. Highly substituted cellulose in which the substituent is a large group forms nematic phases in many solvents. Cellulose with fewer or smaller substituents needs specific solvent interaction in order to form mesophases. Gray and Gilbert [3–6] have given lists of mesophases of solutions of cellulose and its derivatives. Kamide and Saito [7] state that, if cellulose acetate is dissolved in a highly polar solvent, the chain rigidity is enhanced. Also, the size of the solvent might be of importance, the larger solvent molecules inducing more steric hindrance than the smaller. Molecular dynamic simulations of cellulose and cellulose acetate in water and dimethylsulfoxide (DMSO) by Kroon-Batenburg et al. [8] and Kruiskamp [9] revealed that the influence of acetylation is strongly dependent on the solvent. Upon the DS being increased, in water the persistence length shows an increase and subsequent decrease. The reverse holds if DMSO is used as a solvent in the simulations.

As demonstrated by the above overview, to elucidate the rules in mesophase formation of cellulose-based systems, it is important to know the roles of both the solvent and the substituent. As an example we will regard the role of phosphoric acid as a solvent. Isotropic solutions of non-derivatised cellulose in phosphoric acid are known from patent literature and from a review by Turbak [10–13]. Anisotropic solutions of some cellulose derivatives in phosphoric acid and other inorganic acids are mentioned by Kamide et al. in an Asahi patent application and a relevant paper [14,15]. Liquid crystalline solutions of cellulose acetate in phosphoric acid both with a high and a low H_3PO_4-concentration in the solvent are mentioned. A Michelin patent application by Villaine and Janin [16] describes liquid crystalline solutions of cellulose formate in a mixture of phosphoric acid and formic acid. Finally, an anisotropic solution of non-derivatised cellulose in a specific mixture of sulphuric acid (SA), polyphosphoric acid (PPA) and water (W) is described in an Asahi patent

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application and a relevant paper by Kamide et al.[17,18]. It was found that in the case of only one specific composition of the solvent, viz. SA/PPA/W is 1/8/1, an anisotropic solution is formed in a cellulose concentration higher than 16% w/w.

This paper is concerned with the clarification of some phenomena regarding the effects of substitution and solvent on mesophase formation of cellulose acetate in phosphoric acid. The effect of the DS and the role of the acid strength will be examined systematically. As no commercial grades with low and intermediate degrees of substitution at a sufficiently high degree of polymerisation were available, these samples were synthesised by partial saponification of cellulose acetate (DS of approximately 2.5) and cellulose triacetate. The samples were dissolved in phosphoric acids with varying strength, so that liquid crystalline solutions were formed. Upon being heated, the birefringent cellulose acetate solution becomes isotropic. The temperature at which this happens is called the clearing temperature, as described by Picken and Vertogen [19,20]. The solutions were analysed by determining this clearing temperature and the birefringence.

1.2. Phosphoric acid

Phosphoric acid is a special acid in that it can form dimers, oligomers and even polymers. Orthophosphoric acid is the reaction product of phosphorus pentoxide and water. Ullmann [21] gives the distribution of the various acids as a function of P_2O_5 concentration. From the equilibrium distribution the amount of water in the acid system can be calculated. This is displayed in Fig. 1. Here we can see that even above the concentration of the composition of orthophosphoric acid there is still some water present in the system, which is due to dimerisation. Orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$) and polyphosphoric acid ($H_6P_4O_{13}$) correspond to P_2O_5 concentrations of 72.4, 79.6 and 84% w/w, respectively. Compositions between that of ortho- and pyrophosphoric acid are also referred to as superphosphoric acid as defined by Slack [22].

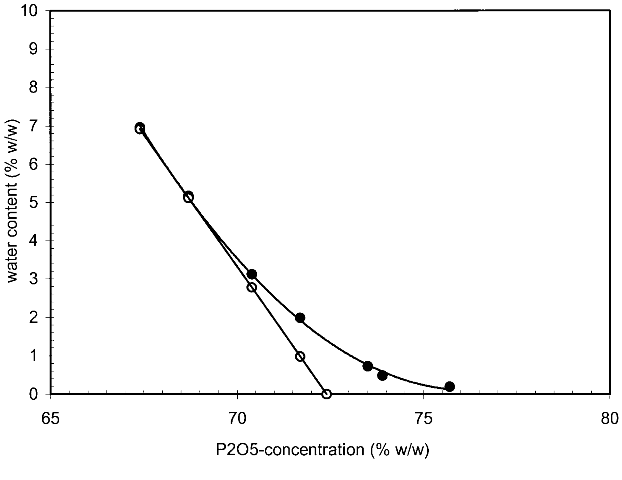

Fig. 1. Water content as a function of P_2O_5-concentration in the solvent, open circles: apparent; solid circles: real, due to the equilibrium.

In this paper, the solvent composition is defined by a P_2O_5 content, the solvent being given by the sum of all the phosphoric acid forms and water, including the equilibrium moisture of the polymer. Therefore, in all cases the moisture content of the cellulose acetate samples is measured. The polymer concentration is then corrected for this equilibrium moisture content, not by drying the polymer in advance but by considering the amount of water to form part of the solvent.

We define a presolvent and a solvent as follows. The presolvent is described by the composition before the addition of the polymer, and is characterised by a P_2O_5 concentration in which the moisture of the polymer is not taken into account. After the addition of the polymer, the solvent comprises all the phosphoric acid components and water. This means that the moisture of the polymer is incorporated in the calculation of the P_2O_5 concentration.

By viewing orthophosphoric acid as part of the P_2O_5-water system, it is now possible to increase the acid concentration and study the effect on the clearing temperature. Phosphoric acid presolvents can be prepared by mixing two or more of the following components: orthophosphoric acid, pyrophosphoric acid, polyphosphoric acid, phosphorus pentoxide and water. Also other acids of pentavalent phosphorus can be used. The solid components will have to be melted, either before or after mixing them with the other substances. Moreover, the system should be allowed to assume its new state of equilibrium.

2. Experimental

2.1. Raw materials

Cellulose acetate and cellulose triacetate were obtained from Fluka. Four batches were used. The DS was determined analytically, according to the method described below, to be 2.74 for batch 1, 2.37 for batch 2, 2.30 for batch 3, and 2.89 for batch 4. According to Fluka specification the molecular weight was 61000 for batch 1–3 (cellulose acetate) and 72000–74000 for batch 4 (cellulose triacetate). Orthophosphoric acid was obtained from La Fonte Electrique SA, Bex Suisse (crystallised, 99% w/w H_3PO_4). Polyphosphoric acid (84% w/w P_2O_5) was delivered by Stokvis.

2.2. Dissolution of cellulose acetate in aqueous orthophosphoric acid and superphosphoric acid

In order to study the influence of the DS, it is desirable to have a wide variety of DS-values. Commercial grades of cellulose acetate are mostly highly substituted. Intermediate values were prepared by hydrolysis of the commercial grades. Cellulose acetate was suspended in an ethanol/water mixture. Partial saponification was performed with an NaOH-solution.

The degrees of substitution of the various cellulose acetate samples were determined according to ASTM specifications [23]. The results were compared with IR spectroscopy. The equilibrium moisture content of the cellulose acetate samples was determined by using a balance equipped with an IR-drier or halogen-drier.

For the influence of the acid strength to be studied solutions of cellulose acetate were prepared both in aqueous orthophosphoric acid and in superphosphoric acid. The presolvents were prepared by mixing in the desired ratio two of the following components: water, orthophosphoric acid, and polyphosphoric acid. Mixing was performed in an IKA duplex kneader during approximately 30 min at about 50°C, to melt the solid component. The presolvent was cooled to approximately 15°C, after which the cellulose acetate (containing approximately 4% w/w equilibrium moisture) was added. The system was kneaded for 30 min, during which the kneader was cooled. White, glossy, fibre-forming solutions were obtained.

Part of the solution was coagulated in water and thoroughly washed. On several of these precipitated polymers the DS was determined. It appeared that the DS decreased only slightly upon dissolution in phosphoric acid: a decrease of 0.17 in DS was observed. From IR measurements in the solutions it appeared that saponification became slightly more pronounced with a decreasing P_2O_5 concentration.

A number of solutions were diluted with the phosphoric acid presolvent for creating a concentration series.

2.3. Determination of clearing temperature and birefringence

The anisotropic cellulose acetate solutions display a bright and occasionally colourful image when viewed under a polarisation microscope. Upon heating the colours start to fade until in the end a dark field appears. At the higher degrees of substitution the solutions of cellulose acetate are birefringent but hardly any colours are observed under the polarisation microscope. But a clearing temperature could still be determined. A Jenaval polarisation microscope (amplification 100 ×) was used. Approximately 100 mg of the solution was applied between two slides. The sample was introduced into a Mettler FP 82 Hot stage and heated at a heating rate of 5°C/min. When the image had turned almost black, the temperature was recorded. This temperature was taken to be the clearing temperature T_c similar to measurements by Picken [19] on aramid solutions.

The birefringence Δn was determined by making use of a type B Abbe refractometer type B, as presented by De Jeu [24] and Picken [25]. Measurements were performed at room temperature. Use was made of a polariser in the ocular of the refractometer to select the parallel and perpendicular refractive index. By measuring the angles of total reflection the two refractive indices were determined. The difference found between the two values was the birefringence.

3. Results and discussion

3.1. Influence of phosphoric acid concentration

Fig. 2 displays the clearing temperatures of the solutions with varying orthophosphoric acid concentration. The acid strength is expressed as the P_2O_5 concentration in the solvent, as defined above. At a P_2O_5 content lower than that of orthophosphoric acid (72.4% w/w) a large influence of acid strength is observed. Anhydrous conditions can be reached by increasing the P_2O_5 content in the solvent. Although the effect of the phosphoric acid concentration on the clearing temperature was very pronounced for a P_2O_5 content below 724% w/w, hardly any influence of the acid strength is found above that level. This can be attributed to the amount of water in the solvent. As water is a small molecule, the molar quantities are rather large as compared with the molar amount of polymer in the solution. Fig. 2 also shows the molar ratio of water and glucose units as a function of the P_2O_5 concentration in the solvent. Now it is more apparent why only a small amount of water is of such a large influence on the clearing temperature, considering that polar groups from the cellulose acetate (either hydroxyl or carbonyl) and water have to compete for the interaction with phosphoric acid.

The importance of water in mesophase formation of solutions of cellulose in a mixture of *N*-methylmorpholine *N*-oxide (NMMO) and water was also recognised by Chanzy et al. [26], who used a molar ratio of NMMO and water to characterise the solvent. However, in this system a defined amount of water is necessary to dissolve the cellulose.

3.2. Influence of cellulose acetate concentration and degree of substitution

Fig. 3 displays the IR-spectra of the various samples of

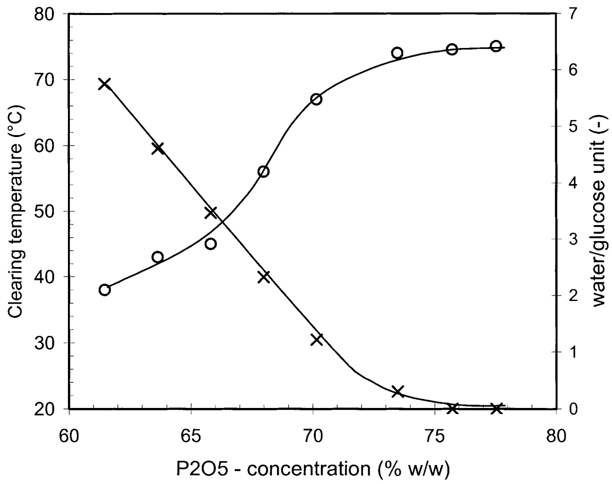

Fig. 2. Influence on clearing temperature of P_2O_5-concentration in the solvent (open circles). Orthophosphoric acid corresponds to P_2O_5 content of 72.4% w/w. The DS was 2.30 and the cellulose acetate concentration 28.2% w/w. Also indicated is the ratio of water and glucose units (crosses).

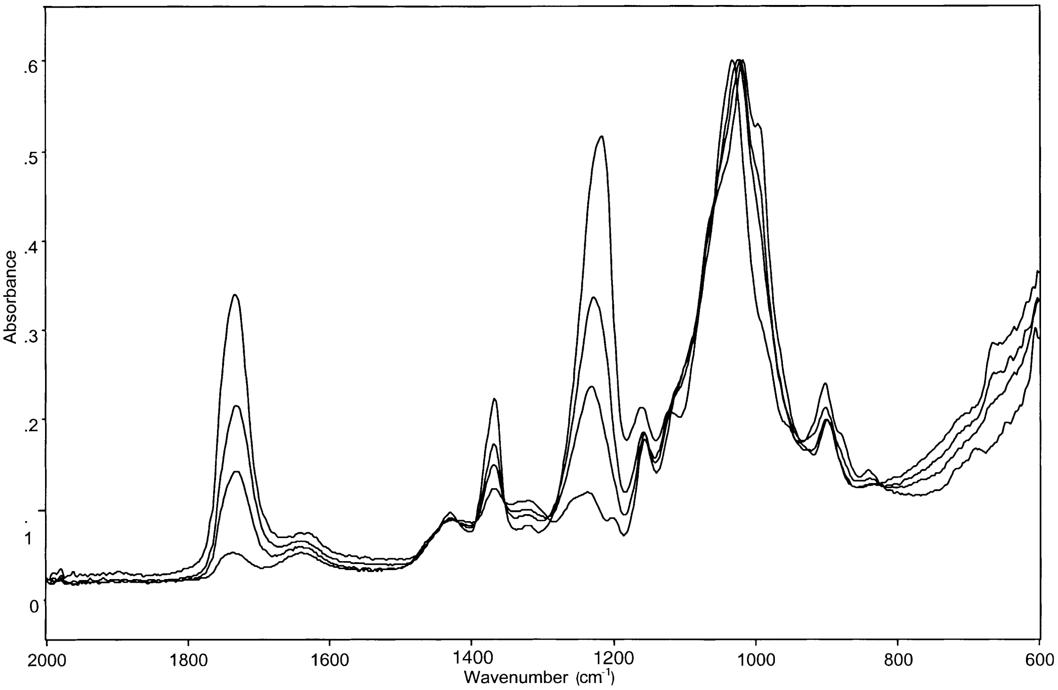

Fig. 3. Infra-red spectra of cellulose acetate samples with the acetate peak at 1735 cm^{-1} for DS-values of 0.23, 0.96, 1.53, and 2.37 (increasing height of the acetate peak).

cellulose acetate that were prepared by partial saponification of the commercial grades. It appears that a broad range of degrees of substitution can be covered by partial saponification. Since the clearing temperature is unaffected by the acid strength at elevated phosphoric acid concentrations, the influence of cellulose acetate concentration on clearing temperature was studied at a high phosphoric acid concentration. In addition the influence of the DS was studied. Fig. 4 displays the influence of cellulose acetate concentration on clearing temperature for three values of the DS.

All lines show a moderate influence of concentration on clearing temperature, with the slope decreasing at increasing concentration, probably due to degradation. Thus plotted, there seems to be a large influence of the DS. However, at a constant polymer concentration the number of chains decreases with increasing DS. This can be taken into account when calculating an equivalent cellulose concentration ($c_{\mathrm{cell,eq}}$) by compensating for the molecular weights of the monomeric units, according to:

$$c_{\mathrm{cell,eq}} = c_{\mathrm{CA}} \frac{162 + \mathrm{DS}42}{162} \qquad (1)$$

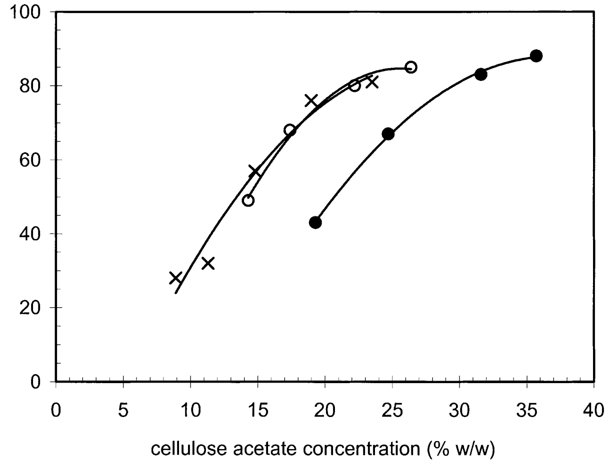

Fig. 4. Clearing temperature as a function of cellulose acetate concentration (crosses: DS = 0.23; open circles: DS = 0.77; solid circles: DS = 2.74) using a presolvent with a P_2O_5 concentration of 74.4% w/w

Fig. 5 displays the clearing temperature as a function of this equivalent cellulose concentration. Now the curves for the various grades coincide perfectly. Thus it seems to be that the influence of the DS will almost vanish when using the equivalent cellulose concentration. The clearing temperature is hardly affected by the DS when considering equal number densities. This is very remarkable and deserved closer examination.

Therefore, the influence of the DS was studied using a constant number density of monomeric units, corresponding to an equivalent cellulose concentration of 15% w/w. Fig. 6 shows the clearing temperature as a function of the DS. It is demonstrated that cellulose acetate can be dissolved in this particular solvent, even when the DS is as low as 0.23. This in itself is amazing; for it is known that the solvent to be chosen depends on the DS of cellulose acetate. At the same equivalent cellulose concentration the clearing temperatures are similar, which justifies the use of a constant number density of monomeric units. The clearing temperature

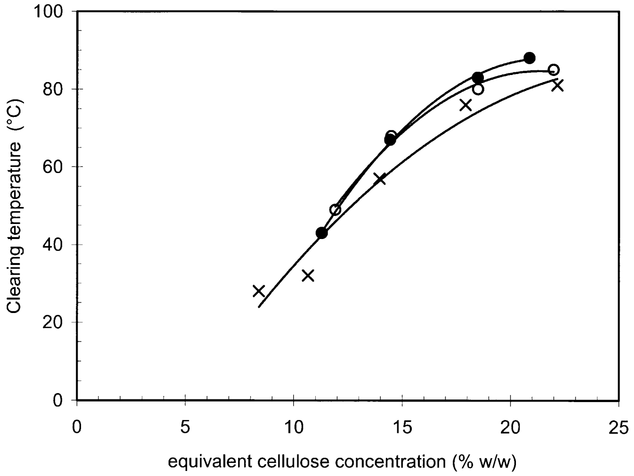

Fig. 5. Clearing temperature as a function of equivalent cellulose concentration (crosses: DS = 0.23; open circles: DS = 0.77; solid circles: DS = 2.74) using a presolvent with a P_2O_5 concentration of 74.4% w/w.

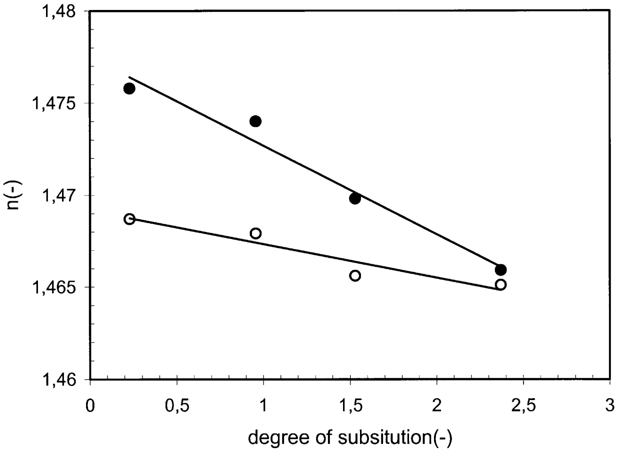

Fig. 7. Influence of DS on parallel (solid circles) and perpendicular (open circles) refractive indices.

increases only slightly upon varying the DS from 0.23 to 2.89, although the polymer concentration will increase from 15.9 to 26.3% w/w.

Fig. 7 shows the parallel and perpendicular refractive indices of the solutions of cellulose acetate with varying DS. The birefringence of the solutions is strikingly low. At the lowest DS the birefringence is 0.005, which is much lower than the birefringence of aramid solutions, as determined by Picken [25] (0.06 for a 10% w/w solution of DABT). The low birefringence of the cellulose acetate solutions is due to the low intrinsic birefringence of the polymer itself. Furthermore, the birefringence strongly depends on the DS, with hardly any birefringence being left in the highly substituted samples. Therefore, when viewed under a polarisation microscope, the image is not spectacular, no colours are observed for the higher DS. However, a phase transition can still be observed upon heating, indicating that the solutions are really liquid crystalline. The DS has a marked influence on the birefringence, but has hardly any effect on the clearing temperature. The decrease of the birefringence is therefore not related to a decrease of orientation in the solvent, but to a decrease of the maximum birefringence of the chains in solution. By substitution the electron density is changed and hence the interaction with light in both directions, which corresponds to the birefringence. This difference in birefringence can also be seen in the fibres of cellulose, cellulose acetate (DS ≈ 2.5) and cellulose triacetate, viz. +0.05, +0.005 and −0.003, respectively, according to Ullmann [27]. Hence, for cellulose triacetate the birefringence is even negative. The same trend is now observed for the solutions in phosphoric acid. In that case a change in birefringence is therefore not related to a change in orientation but is caused by a change in internal structure of the molecule. Another solvent often used for cellulose acetate is trifluoroacetic acid, from which highly oriented cellulose acetate yarns were spun, which were saponified to very strong cellulose yarns by O'Brien [28,29]. In Fig. 8 a comparison is made between cellulose triacetate dissolved in phosphoric acid and cellulose triacetate dissolved in trifluoroacetic acid, as measured by Dayan et al. [30]. It is shown that when dissolved in phosphoric acid cellulose triacetate displays anisotropy at much lower mass concentrations than when dissolved in trifluoroacetetic acid. Part of the difference can be ascribed to a difference in density of the solvent, viz. 1900 kg/m^3 for phosphoric acid and 1540 kg/m^3 for trifluoroacetic acid, if an excluded volume approach is used for explaining the occurrence of a liquid crystalline phase. However, even when using volume fractions rather than weight fractions, cellulose triacetate still forms an anisotropic phase in superphosphoric acid at lower polymer concentrations than in trifluoroacetic acid. This offers interesting opportunities for the use of such solutions, e.g. for the preparation of highly oriented fibres. Of course, from an environmental perspective phosphoric acid is preferred to trifluoroacetic acid.

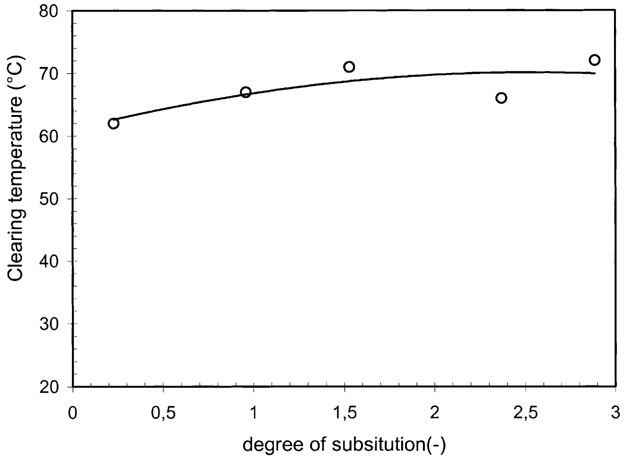

Fig. 6. Influence of DS on clearing temperature at an equivalent cellulose concentration of 15% w/w and P_2O_5 concentration in the presolvent of 74.4% w/w.

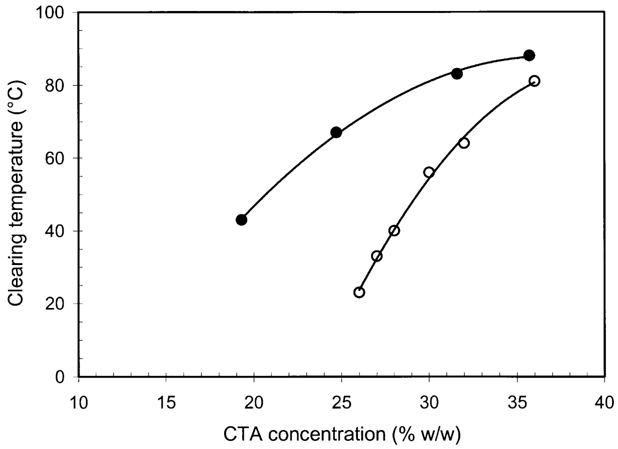

Fig. 8. Comparison between clearing temperature of cellulose triacetate (CTA) solutions in phosphoric acid (solid circles) and trifluoroacetic acid (open circles, data from Dayan [30]) both determined by means of polarisation microscopy.

4. Discussion

It was demonstrated that whereas the water content in solutions of cellulose in phosphoric acid plays a major role in the formation of a liquid crystalline phase, the degree of acetylation is of minor importance. This is rather surprising in that in the formation of mesophases of cellulose the stress has always been on the role of derivatisation. As formulated by Gray [3] strongly acidic or polar solvents, however, promote the formation of such phases, reducing the importance of the nature and the amount of substituents. The latter statement has been confirmed in the present work. As a matter of fact, the DS is of lesser significance considering the number density of chains in the solution. To that end an equivalent cellulose concentration has been defined. We can compare the experimental results with theories on the subject. Consider a chain with a Kuhn length L_k and a diameter d. Both in the Onsager [31] and in the Flory [32,33] approach the critical volume fraction ϕ' is inversely proportional to the axial ratio x ($= L/d$)

$$\phi' \propto \frac{1}{x} \tag{2}$$

Suppose that the Kuhn length and thus the chain flexibility is unaffected by the substitution, then the critical volume fraction scales with the molecular weight of the monomeric unit of the cellulose acetate (M_{mon}) as:

$$\phi' \propto \frac{d}{L_k} \propto M_{\mathrm{mon}}^{1/2} \tag{3}$$

The critical equivalent cellulose concentration ($c^*_{\mathrm{cell,eq}}$) relates to the critical volume fraction as:

$$c^*_{\mathrm{cell,eq}} = c^*_{\mathrm{CA}} \frac{162}{M_{\mathrm{mon}}} = \phi' \frac{\rho_{\mathrm{pol}}}{\rho_{\mathrm{sol}}} \frac{162}{M_{\mathrm{mon}}} \tag{4}$$

Assuming constant densities of the polymer ρ_{pol} and of the solution ρ_{sol} the critical equivalent cellulose concentration scales with the molecular weight of the monomer as:

$$c^*_{\mathrm{cell,eq}} \propto M_{\mathrm{mon}}^{-1/2} \tag{5}$$

To give an example: in accordance with this rough estimate the ratio of the critical equivalent cellulose concentrations at a DS of 0.23 and of 2.74 is 1.3. Therefore, in this approach the effect of substitution on the critical equivalent cellulose concentration is not very pronounced. In the experiments, however, an even smaller difference was found; but the Kuhn length will probably be affected by substitution, and solvatation effects will also play a role. The last effect can be taken into account by considering d the diameter of the solvated polymer instead of that of the polymer chain itself.

Another line of theories is based on mean-field theories by Maier and Saupe [34,35], which were modified for application to polymers by Picken [19]. In that approach the so-called coupling constant determinative of the orienting potential is related to the anisotropy of the polarisability. Therefore, it is remarkable that whereas the clearing temperature hardly depends on the DS, the birefringence, which is related to this anisotropy of the polarisability, is strongly influenced. Later on, the theory turned into a phenomenological one, the original meaning of the coupling constant in the Maier–Saupe theory being abandoned.

Furthermore, water is the critical component in the formation of a liquid crystalline phase in that it has a detrimental effect. Possibly, this is due to the fact that cellulose acetate competes with water for the interaction with phosphoric acid. Thus, the solvent quality is decreased causing a less extended chain.

5. Conclusions

It has been shown already by Kamide et al. [14,15] that cellulose acetate could be dissolved in phosphoric acid. But in the present paper we have studied the influence of substituent and solvent separately. It is demonstrated that cellulose acetate can be dissolved in phosphoric acid with widely varying acid concentrations. Water appears to have a detrimental effect on the anisotropy of the solution.

Cellulose acetate samples have been prepared in a wide range of degrees of substitution by partial saponification. Good solubility in superphosphoric acid was observed over the entire range, which is remarkable in itself; for in other solvents the solubility strongly depends on the DS: in organic solvents solubility only occurs in very narrow ranges of the DS.

It was demonstrated that the best way of studying the influence of the DS is to consider a number density of monomers. When a constant number density of monomers was dissolved the clearing temperature varied only slightly with the DS.

Acknowledgements

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