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Investigation of Solutions of Cellulose

S.N.Danilov, T.I.Samsonova, and L.S.Bolotnikova

This review deals with studies of cellulose solutions. Various solvents for cellulose are characterised in detail. On the basis of the experimental results it is concluded that stable compounds are formed as a results of the reaction of cellulose with complex-containing solvents. The part played by complexes and alkalis present in the solvent in the dissolution of the cellulose is shown.

Various methods of fractionation and the principal relations between the characteristic viscosity and molecular weight of cellulose in various solvents are considered.

In the section dealing with the dimensions and form of the cellulose macromolecules it is shown that cellulose is of much greater dimensions than flexible synthetic polymers, owing to the greater size of the monomeric unit, the considerable extension of the macromolecules in the solution, and the reaction of cellulose with the solvent.

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1. SOLVENTS FOR CELLULOSE

The peculiarities of the structure of cellulose macromolecules, the regularity of its structure, and the strong intermolecular interactions, are due to the presence of hydrogen bonds, which results in cellulose being insoluble in water and organic solvents. It is soluble in aqueous solutions of complexes of bivalent and tervalent metals, certain salts, and concentrated acids (phosphoric acid).

The most widely used of the solvents containing complexes is a solution of the amminecopper complex, first obtained by Schweizer in 1857.[1] This solvent contains compounds formed in the reaction of copper hydroxide with ammonia and of the general formula $Cu(NH_3)_m(OH)_2$, with the tetramminecopper complex $Cu(NH_3)_4(OH)_2$ predominating.

When this solvent is stored in air for even a rather short period there is a change in composition owing to oxidation of ammonia to nitrous acid and beyond, as is shown by the appearance in the solution of ammonium nitrates and nitrites on storage[2] and the copper concentration drops owing to the separation of copper hydroxide. Danilov and coworkers[2-4] investigated the processes in the oxidation of amminecopper solutions of cellulose. In these solutions oxygen attacks both the ammonia and the cellulose as a vigorous carrier of oxygen is present—the copper ion in the tetrammine complex[5,6].

The oxidation of both the solvent itself and of solutions of cellulose in it can be suppressed by the introduction of additions of organic (sucrose, glucose, mannitol, tartaric acid) or inorganic (sulphite, thiosulphate) substances. These additions stabilise the amminecopper complex and lessen the oxidisability of the ammonia. The oxidative degradation of cellulose in a solution of amminecopper complex can be prevented by the addition of metallic copper to the solution, as this vigorously bonds the oxygen[6-12]. Additions of inhibitors greatly reduce the oxidisability of cellulose but do not eliminate it.

Cellulose concentrations of only 3–4% can be obtained by direct dissolution of cellulose in a solution of the amminecopper complex. To prepare more concentrated solutions, cellulose is mixed with a basic copper salt and ammonia solution. As the cellulose dissolves, additional amounts of the basic copper salt pass into the solution. Cellulose solutions with a concentration of over 12% can be obtained in this way. Foreign ions have a considerable effect on the solubility of basic copper salts in ammonia. Thus, copper hydroxide dissolves better in ammonia in the presence of sodium and ammonium sulphates[7].

Traube[12] obtained the ethylenediaminecopper complex by replacing ammonia by ethylenediamine (ED). This system is more stable than the solution of the amminecopper complex and there is less oxidation of solutions of cellulose in it. However, the solubility of cellulose in solutions of the ethylenediaminecopper complex is less than in solutions of the amminecopper complex[13]. According to Marx[14] the maximum possible concentrations of cellulose of various degrees of polymerisation reach 0.6–1.2 g per 100 ml on varying the degree of polymerisation from 6000 to 1500.

Unlike amminecopper solution, where a large excess of ammonia is used, solutions of the ethylenediamine complex dissolve cellulose at a strictly definite ratio of ethylenediamine to copper, en : Cu, which should be 2.[12,15] In instances when this ratio exceeds 2, that is, the en solution is not saturated with copper hydroxide, the solubility of cellulose is less. Since the solvent should always have a strictly defined composition this complicates its preparation. The information about the variation of the characteristic viscosity $[\eta]$ with the composition of the solution of ethylenediaminecopper complex is rather contradictory. Thus, Marx[14] thinks that the en : Cu ratio can be varied from 1.69 to 2.75 (0.5 g-ion copper/litre) without affecting the viscosity. According to Wilson[15], en : Cu should lie within the limits 2.00 ± 0.04, and the copper concentration 1.00 ± 0.1 M, for the change in relative viscosity not to exceed 1%. In studying the formation of the ethylenediaminecopper complex in aqueous solution, Vink[16] found that the existence of complexes of composition $Cuen_2^{2+}$, $Cuen^{2+}$, and $Cuen_3^{2+}$ is possible. He showed that at the ethylenediamine : copper ratio of 1.82 the following complexes can exist in the solution: $Cuen_2^{2+}$ 69.5%, $Cuen_2OH^+$ 9.3%, $Cuen(OH)_2$ 21.2%, that is, the complex $Cuen_2$ predominates

in the solution. Like the solutions of amminecopper complex, solutions of the ethylenediaminecopper complex are unstable, although to a lesser degree[17,18]. Measurement of the viscosity of cellulose in solutions of the ethylenediamine complex also must be done in the absence of atmospheric oxygen[18].

Vink[19] observed, in studying the kinetics of oxidative destruction of cellulose in a solution of the ethylenediaminecopper complex, that the cellulose concentration has no effect on the rate of destruction. The rate is a maximum in the first day after the preparation of the solution but then decreases, owing to the formation of inhibitors in the ethylenediaminecopper solution. Two compounds were isolated: glyoxal dioxime HO–N=CH–CH=N–OH and hydroxyiminoacetic acid HO–N=CH–COOH. In investigating these and other oximes it was observed that hydroxyiminoacetic acid has the greatest inhibiting action. In addition to inhibitors, accelerators of the oxidation were found—dimethylglyoxime. It is noteworthy that ethylenediamine itself is not oxidised by oxygen; its oxidation, leading to the formation of inhibitors, takes place only in the presence of copper.

The use of solutions of ethylenediaminenickel[20] and ethylenediaminecobalt[21] complexes as solvents does not have any advantages over the ethylenediaminecopper complex. The presence of nickel and cobalt ions, which can be oxidised from the bivalent to the tervalent state, increases the destruction of the cellulose. Furthermore, these solvents are unstable and they are made in an atmosphere of nitrogen, to avoid the formation of cobalt(III) and nickel(III) hydroxides, which give complexes with ethylenediamine which do not dissolve cellulose. The solubility of the latter in these solvents is low.

Ethylenediamine also forms a complex with zinc and the aqueous solution of this compound dissolves cellulose[22,23]. However, the solvent is stable only at low temperatures.

Unlike the above solvents an aqueous solution of the ethylenediaminecadmium complex[24,25] (Cadoxene) is stable for an almost unlimited time, but cellulose does not oxidise much in it[26,27].

A solution of the ethylenediaminecadmium complex was first obtained in 1957 by Jayme[24,25] by saturating ethylenediamine solutions of various concentrations with basic cadmium salts, cadmium hydroxide at low temperatures, or cadmium oxide at room temperature and at 3–7°C.[28] This can be used as a solvent for cellulose with polymerisation degrees < 1200. To improve the dissolution of the cellulose, Jayme[29] suggested the preliminary swelling of the cellulose in water, but Henley[30] increased the solubility of cellulose by the addition of 0.2–0.5 mole sodium hydroxide to the Cadoxene. It is then possible to dissolve cellulose with a polymerisation degree of 5500. The maximum concentration of cellulose with degree of polymerisation 1200 reaches 4%. Nadziakiewics and Jedlinska[31] also added sodium hydroxide to the solution to improve the solubility of cellulose. However, addition of sodium hydroxide leads to an increase in the destruction of cellulose in Cadoxene[28,32].

Donetzhuber[33] showed the advantage of using a low temperature in the dissolution of cellulose in Cadoxene.

Bolotnikova and Samsonova[34,35] obtained Cadoxene which dissolves cellulose with degree of polymerisation 2000, by saturating a solution of ethylenediamine with cadmium oxide at 0°C for 1 h. In the dissolution of cellulose with a degree of polymerisation > 5000 it is desirable to reduce the temperature to between 0° and −50°C. The maximum concentration of cellulose at DP $\simeq$ 1200 is 6–7%.[36]

Cellulose undergoes comparatively little oxidation in a solution of the ethylenediaminecadmium complex[26,34,37]. The presence of foreign ions (Cu^{2+}, Co^{2+}, Fe^{3+}, Ni^{2+}) as impurities accelerates the destruction of cellulose[37], therefore cotton cellulose is oxidised less than sulphite.

Among other methods for making Cadoxene that of Reimers[38] merits note. Ethylenediamine is passed through a column filled with a mixture of sand and cadmium oxide. A solution of the ethylenediaminecadmium complex of the desired cadmium concentration is obtained after 15 min.

An alkaline solution of sodium tartratoferrate complex is another solvent which is used for cellulose. Frank[39] was the first to investigate the complex present in this solvent. The formation of two complexes is possible in the FeIII–tartaric acid–NaOH system, $[(C_4H_2O_6)Fe]Na$ and $[(C_4H_3O_6)_3Fe]Na_6$ at $Fe(OH)_3$: tartaric acid : NaOH molar ratios of 1 : 1 : 1 and 1 : 3 : 6 respectively. Jayme and Verburg[40] found the compositions of mixtures of components with the greatest dissolving power; the complex $[(C_4H_3O_6)_3Fe]Na_6$ is formed. The Na in this can be replaced by K and Li,[41] but the replacement of the tartaric acid by other organic acids: malic, oxalic, lactic, citric, or salicylic, does not lead to the formation of complexes which dissolve cellulose, since the complex is precipitated when the alkali is in excess[42].

Jayme and Bergman[43] proposed two methods for the preparation of a solution of sodium tartratoferrate complex (STFC). The reaction of stoichiometric amounts of an iron(III) salt and tartaric acid in the presence of an excess of sodium hydroxide gives the complex $[(C_4H_3O_6)_3Fe]Na_6$, which is separated by precipitation with alcohol. Then this very hygroscopic complex dissolves in the alkali solution and sodium tartrate is added for stabilisation. However, the most widely used method for making STFC is from tartratoferric acid, insoluble in water[43]. This is dissolved in a solution of alkali and sodium hydrogen tartrate, and the sodium hydrogen tartrate is added in slight excess to stabilise the solution. Two STFC solutions are used for dissolving cellulose with a high degree of polymerisation: one which brings about the swelling of cellulose contains 300 g litre^{-1} STFC, 1.0 N NaOH, and 35 g litre^{-1} sodium tartrate, and the composition of the second solution is 480 g litre^{-1} STFC, 3.0 N NaOH, and 25 g litre^{-1} sodium tartrate. On mixing these two solutions a solvent with optimal dissolving ability is obtained[44]. Valtasaari[45] obtained an alkaline solution of STFC by a simplified method—mixing iron nitrate, tartaric acid, and sodium hydroxide without isolating the pure complex. However, this solvent is suitable only for dissolving cellulose with a degree of polymerisation up to 1500, since foreign ions in this solvent reduce the solubility of cellulose[46]. All other methods for making STFC are only modifications of the methods of Jayme, Bergman, and Valtasaari[47–50]. Solutions of cellulose in an alkaline solution of STFC are fairly stable[51–54]; $[\eta]$ for sulphite cellulose with a degree of polymerisation of 1400 did not change in two days[53], there is only a change in the slope of the relation $\eta_{sp}/c = f(c)$, where c is the concentration in g/100 ml and η_{sp}/c is the reduced viscosity, which shows a change in the interaction of cellulose with the solvent. After 4 days $[\eta]$ had changed by $\sim$ 6%. An investigation of the kinetics of destruction of cellulose in STFC solution[54] showed that it does not depend on the concentration of cellulose in the solution but increases with the temperature. The rates of destruction of cellulose in STFC solution in an atmosphere of nitrogen, air, and oxygen are in the ratio 1 : 3 : 9. An analysis of the oxidation products of cellulose by gas chromatography showed that the oxidation takes place mainly at carbon atoms 2 and 3. Jayme and coworkers[55] later found rather pronounced destruction of cellulose in STFC solutions.

An alkaline solution of biuretcopper complex in which cellulose can also dissolve is formed on mixing copper hydroxide and biuret in 1 : 2 ratio in the presence of potassium hydroxide [56]. Increasing the copper : biuret ratio from 2 to 4 leads to a decrease in the solubility of the cellulose. On replacing the potassium hydroxide by sodium hydroxide the biuretcopper complex dissolves more slowly and to a lesser extent. The solvent is unstable. On storing it for 2–3 weeks the odour of ammonia appears, indicating decomposition of the biuret. The presence of cellulose in the solution of the complex accelerates its decomposition although the solubility of cellulose is unchanged. This is probably because an amminecopper complex is formed in the decomposition of the biuretcopper complex. There has not been a quantitative study of the stability of solutions of cellulose in the biuretcopper complex, although Jayme and Lang [56] noted a significant decrease in the viscosity of cellulose solutions during storage.

As has been shown [57–59], quaternary ammonium bases with a molecular weight over 150 dissolve cellulose, and those with a lower molecular weight cause it to swell. Each organic base can dissolve cellulose only at a definite concentration of the base in water, and this concentration is less the higher the molecular weight of the base. Tetramethylammonium hydroxide (M = 91) and trimethylpropylammonium hydroxide (M = 119) do not dissolve cellulose at any concentration. Tetraethylammonium hydroxide at a concentration of 35–40% in water dissolves cellulose with $M < 250\,000$. The best solvents are the quaternary ammonium bases containing benzyl radicals [59].

Of the other solvents for cellulose mention must be made of phosphoric acid and sodium hydroxide, but their use is limited, since they only dissolve cellulose with moderate degrees of polymerisation. 82–84% solutions of phosphoric acid have been proposed for the dissolution of cellulose by Ekenstamm [60,61]. In studying the effect of various conditions on the solubility of cellulose in phosphoric acid, Danilov and Gintse [62] found that the solubility curve has two maxima, between which there is a region of incomplete solubility. The position of these maxima correspond to the concentrations of acid at which it exists in the form of monohydrate and hemihydrate. When preliminary swelling of the cellulose in water or dilute phosphoric acid is employed dissolution also takes place in the range of compositions between the maxima. Drawbacks of phosphoric acid as a solvent are its own high viscosity and the fact that it can only dissolve celluloses with polymerisation degrees in the range 700–800, or at lower temperatures degrees of polymerisation up to 1200–1500. [60,61]

At a concentration of 10–12% sodium hydroxide can dissolve specimens of cellulose with a degree of polymerisation up to 350. Solutions of cellulose in alkali undergo strong oxidative destruction [4,63–65].

Cellulose dissolves when heated in solutions of certain salts, such as lower chlorides and thiocyanates, but solutions of cellulose in salts have hardly been investigated.

A quite recent proposal [66] was to dissolve cellulose and other polysaccharides in *NN*-dimethylformamide and *NN*-dimethylacetamide to which N_2O_4 and NOCl have been added. To dissolve cellulose in dimethylformamide the molar ratio of N_2O_4 to cellulose must be greater than 3 : 1 and the ratio of NOCl to cellulose greater than 8 : 1. The cellulose is first suspended in the dimethylformamide and then N_2O_4 or NOCl introduced. In contact with moist air cellulose is precipitated. Cellulose can be isolated from these solutions with water or lower alcohols. In the absence of moisture solutions of cellulose in these solvents are stable.

2. INTERACTION OF CELLULOSE WITH SOLVENTS WHICH CONTAIN COMPLEXES

In dissolving cellulose it is necessary to break the strong intermolecular interactions due to a large number of hydrogen bonds. The weakening of the intermolecular interaction is facilitated by solvation—the reaction of the hydroxyl groups of the cellulose with the solvent with the formation of a monosolvate sheath [67–69]. However, the hydrogen bonds in cellulose are not destroyed completely during solvation. On using solvents which contain complexes of metals a compound of cellulose and the solvent is formed and this together with hydration leads to the breaking of the hydrogen bonds and dissolution of the cellulose.

The greatest number of studies has been devoted to elucidating the mechanism of the dissolution of cellulose in a solution of the amminecopper complex. The first investigations in this direction were made by Traube [70–72] who studied the reaction of the amminecopper and ethylenediaminecopper complexes with tartaric acid and glycerol. He applied the results of his investigations to cellulose and suggested the existence of a complex of cellulose and the amminecopper compound of composition $[(C_6H_8O_5)_2Cu][Cu(NH_3)_4]$, where the ratio $C_6H_{10}O_5 : Cu = 2 : 1$. However, this does not fit in with modern views about the coordination numbers of copper. Hess and Messmer [73,74] also thought that the dissolution of cellulose in a solution of amminecopper complex yielded a compound of the alkoxide type, $[C_6H_7O_5Cu]_2[Cu(NH_3)_4]$, in which copper is present in both the anion and the cation. The formation of an alkoxide compound of copper with cellulose was not demonstrated by these investigators and is not very probable. Their papers do not give any evidence of a different type of bonding of the copper in the cation and anion [75].

Danilov and Okun' [76–77] investigated amminecopper solutions of cellulose, hydroxyethylcellulose, methyl cellulose, alginic acid, sugars, and polyhydric alcohols. The investigation of electrophoresis and ionic exchange on cation- and anion-exchange resins, and also the study of the composition of precipitates obtained from solutions of cellulose in the amminecopper complex, the investigation of the absorption spectra of a solution of the amminecopper complex, cuprophane and Cellophane films, and solutions of cellulose and other polyhydroxy-compounds showed that copper is not present in the anion. Copper was deposited only on the cathode and exchange of ions on the anion-exchange resin was not observed, whereas the copper and ammonia were completely absorbed on the cation-exchange resin and cellulose was precipitated.

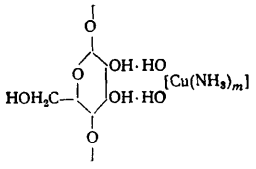
On the basis of their experimental results, Danilov and Okun' concluded that the compound formed in solutions of cellulose in amminecopper complex is not an alkoxide but a molecular compound of variable composition:

$$(C_6H_{10}O_5)_x[Cu(NH_3)_m(OH)_2]_y(H_2O)_z.$$

From a study of the optical rotation and electrical conductivity of amminecopper solutions of 17 glucosides, Reeves [78] suggested that in the solution a cyclic complex is formed between tetra-amminecopper and neighbouring hydroxyl groups of the glucosides. Glucosides without a glycollic grouping do not dissolve in the amminecopper complex.

To find the composition of the compound which is formed in the dissolution of cellulose in a solution of the amminecopper complex, Arkhipov [79] used polarimetric and conductometric methods and also determined the change in the copper concentration on the introduction of cellulose into

the water–ammonia–copper hydroxide system. Thermodynamic quantities were calculated: the equilibrium constant of the reaction, the heat of reaction, the free energy change, and the change in entropy of the system. All these results show the formation of a molecular compound:



The nature of the reaction of cellulose with the ethylenediaminecopper complex is thought by Traube[71] and Jolley[80] to be analogous to interaction with the amminecopper complex.

Gralen and Linderot[81] used a spectrophotometric method to determine the optical density of solutions of glucose in solutions of amminecopper and ethylenediamine complexes at wavelength 330 mμm and various molar volumes of the components. These results were compared with optical densities of solutions of the components. Maximal difference in the optical densities was obtained at the glucose : copper ratio of 1 : 1 for solutions of glucose on the amminecopper complex and 4 : 6 for solutions of glucose in the ethylenediamine complex. Gralen and Linderot considered that these results confirmed Hess's alkoxide formula.

Comparatively recently Vink[82] investigated the formation of polysaccharidemetal complexes in solutions of cellulose in ethylenediaminecopper and ethylenediaminecadmium complexes. He subjected the cellulose solutions, diluted with water, to dialysis through Cellophane membranes. The difference in concentration of ethylenediaminecopper complexes on the two sides of the membrane was determined spectrophotometrically. Cellulose and dextran were used. The latter is soluble in water and therefore the composition of the ethylenediaminecopper complex can be varied within wide limits. The use of cellulose is limited to a narrow range of solvent compositions in which it can be dissolved. All the main experiments were made with dextran and then the results of these experiments were extended to cellulose.

Vink began from the assumption that the reaction of cellulose and dextran with ethylenediaminecopper complex can be effected either by the formation of a complex:

$$R'(OH)_2 + Cuen_2^{2+} + 2OH^- \rightleftharpoons R'O_2Cuen + en + 2H_2O, \quad (1)$$

or by the scheme:

$$ROH + OH^- \rightleftarrows RO^- + H_2O. \quad (2)$$

The degree of bonding β' of the metals, in this instance copper, was calculated by the formula:

$$\frac{\beta'}{1-\beta'} = K_1[OH^-] + K_2\frac{[Cuen_2^{2+}][OH^-]^2}{[en]}, \quad (3)$$

where the values of the equilibrium constants K_2 and K_1 determine the relative importance of reactions (1) and (2).

The degree of bonding of the ethylenediaminecopper complex is almost independent of the concentration of the polymer in the solution, although it is somewhat higher for dextran than for cellulose. It was found that at low concentrations of ethylenediamine in the solution (up to 6%) the predominant reaction is the formation of a complex by reaction (1). On increasing the ethylenediamine concentration the second term in Eqn. (3) decreases and complex formation is replaced by reaction according to Eqn. (2), represented by the first term in the right-hand side of Eqn. (3). Cellulose dissolves in ethylenediaminecopper complex at the ratio en : Cu = 2 (6% ethylenediamine, copper concentration 0.5 M). On increasing the en concentration the ethylenediaminecopper complex does not dissolve cellulose. At high ethylenediamine concentrations (~ 25–40%) and a copper concentration of $\lesssim$ 0.35 M dissolution of cellulose again takes place, which shows the active role of en in the dissolution mechanism.

For solutions of cellulose and dextran in cadmiumethylenediamine complex it was found that within the limits of experimental error the rate constant of the reaction for complex formation is 0. Vink concluded that a complex of cellulose and Cadoxene is not formed, but formation of a compound by reaction (2) occurs. The degree of bonding of cadmium is lower than that of copper, and is the same for cellulose and dextran.

Lindberg and Swan[83] studied the composition of the compound formed in a solution of cellulose in Cadoxene by using the same method as Reeves[78], that is, they studied the change in the optical rotation of solutions of several glucosides and xylosides in Cadoxene and in a 28% solution of en. They think that a complex is formed between the hydroxyls of cellulose and the Cadoxene. A change in the optical rotation of the solution after it had been stored for 24 h was noted. No suggestions were made as to whether this is the consequence of the destruction of the cellulose in the solution or of a change in the state of the solution. A study by paper electrophoresis of a solution of methyl-β-D-glucopyranoside and of several sugars in 10% aqueous solution of Cadoxene (0.55% Cd) showed their low electrophoretic mobility, in good agreement with the results of electrophoresis in aqueous solutions of NaOH.[84]

Vink[82] suggests that the mechanism of dissolution of cellulose in Cadoxene is similar to the mechanism of its dissolution in quaternary ammonium bases. The large $Cden_3^{2+}$ ion in permeating into the cellulose causes its swelling and dissolution. The free ethylenediamine can form molecular compounds with cellulose[85,86].

Jayme and Verburg[41] studied the dissolution of cellulose in alkaline solutions of the sodium tartratoferrate complex[41]. They suggested that the solubility is determined by the swelling of cellulose in NaOH, which in the presence of STFC is so pronounced that dissolution takes place. In carrying out sedimentation and diffusion measurements, Jayme and coworkers[51] started from the fact that reaction between cellulose and STFC ends in addition. By measuring the vapour pressure it was shown that on adding cellulose to the solvent the activity of its components falls. Valtasaari[45] explained the solubility of cellulose in STFC by the direct combination of the cellulose with the iron. Bayer and coworkers[87] studied complex formation in the tartratoferric acid–alkali system from the change in optical rotation and light absorption as a function of the molar ratio of the components. It was found that the optimal Fe^{3+} : tartrate ratio for complex formation is 1 : 4.5. However, a system of this composition does not dissolve cellulose. For good dissolution of cellulose the Fe : tartrate ratio should be 1 : 3. This solution is stable but it contains insufficient tartrate for the complete saturation of the coordinate bonds of the iron. In place of the missing tartrate, water molecules and possibly hydroxide ions from the alkali are bonded with the iron. In the dissolution of cellulose the hydroxyl groups at carbon atoms 2 and 3 displace water molecules and hydroxide ions and form a new chelate compound. In this the hydrogen bonds of the cellulose are broken, destroying the physical structure, and the cellulose enters the solution. Tartrate ions are not displaced from their compounds with iron.

The general structure of the complex, which consists of iron and tartrate ions and of cellulose, cannot be found at present as the nature of the structure existing in the solvent is not known accurately.

3. FRACTIONATION OF CELLULOSE

The molecular weight distribution of cellulose is now mainly determined by the fractionation of its nitrates[88-91]. However, the fractionation of cellulose nitrate under conditions under which the usual polymers are fractionated leads, as Marx showed[92], to destruction, and this is the greater the higher the molecular weight[93]. The fractionation of cellulose nitrate is a long operation and takes 7–10 days. This is also insufficient, since the destruction of cellulose nitrate increases the longer the solution is kept. The breakdown is accelerated by rise in temperature and by alkali metal ions leached out of the glass[93]. In addition it is difficult to obtain completely substituted cellulose nitrate and therefore during fractionation separation will take place both by molecular weights and by degrees of substitution. Therefore it is important to carry out the fractionation of the cellulose by a direct method. Attempts were made to use all the present solvents for the fractionation of cellulose.

In the fractionation by the dissolution method a change in the solubility of cellulose in solutions of alkalis is brought about either by reducing the temperature from 20° to −12°C[94-96] or by change in the alkali concentration[97]. Acetone was used as precipitant in the fractionation of solutions of cellulose in alkalis by the precipitation method[98]. But only cellulose of a moderate degree of polymerisation is soluble in alkali and in alkaline medium it undergoes marked destruction in the presence of air.

Phosphoric acid can be used as solvent in the fractionation of cellulose of moderate degree of polymerisation. The method is based on the fact that at phosphoric acid concentrations from 72 to 83% macromolecules of cellulose of different sizes are dissolved[61]. The solubility of cellulose in phosphoric acid depends on the temperature and increases as the temperature is reduced[99]. According to Akim[100], who studied the polydispersity of celluloses by their fractional dissolution in phosphoric acid, seven or eight fractions can be obtained in 3–4 h. In the fractionation of cellulose in phosphoric acid solutions hydrolysis of cellulose is possible.

The method of fractionating cellulose from its solutions in sulphuric acid[101] is based on the ability of cellulose to be precipitated from such solutions at temperatures from −15° to −20°C on varying the concentration of the acid. A drawback of this method also is the pronounced hydrolysis brought about by the action of sulphuric acid and the possibility of obtaining a total of three or four fractions.

In the fractional dissolution of cellulose in solutions of amminecopper and ethylenediaminecopper complexes a change in the solubility of the cellulose was brought about[102] by the use of amminecopper solutions with different copper concentrations. Coppick and coworkers[98] and Müller and Rogers[103] separately treated several specimens of cellulose with a constant volume of solvent but with different copper concentrations, and Shulyatikova and Mandel'baum[104] varied the absolute amount of copper in the solvent used for dissolving the cellulose. In all the above instances it is thought that dissolution of cellulose with different degrees of polymerisation depends on the concentration of copper in the solution.

Sihtola and coworkers[105] checked this in the following manner. Different amounts of ammonia were added to a solution of cellulose in amminecopper complex, and the concentration of copper in the solution was altered, during which part of the cellulose was precipitated from the solution. Then its characteristic viscosity was determined. Another part of the cellulose left in the solution was precipitated with acid and $[\eta]$ was again measured. It was thus shown that although the concentration of copper in the solution was varied the characteristic viscosity of the precipitates hardly altered, that is, fractional separation did not occur.

The precipitants used for the fractional precipitation of cellulose from its ethylenediammine copper solutions are acids[106] and organic substances (glycerol, propanol, ethanol).[105] As Sihtola and coworkers[105] showed, breakdown of the complex occurs if acid is used to precipitate the cellulose. Usually three or four fractions are obtained, the first of which contains about two-thirds of the weight of the cellulose taken for fractionation. When glycerol and propanol are used to precipitate cellulose from its ethylenediaminecopper solutions the fractionation occurs according to molecular weights. However, it was concluded[105] that solutions of cellulose in the ethylenediaminecopper complex cannot be used for fractionating the cellulose with the aim of determining its molecular weight distribution, owing to the destruction of the dissolved cellulose by atmospheric oxygen.

In recent years Jayme and coworkers used the method of fractional dissolution for fractionation of cellulose from its solutions in Cadoxene[28] and an alkaline solution of the sodium tartratoferrate complex[107]. This was done by adding solvent with various cadmium contents to known weights of cellulose. After shaking for a fixed period the insoluble part was separated by centrifuging. Cellulose was precipitated from the solution left after centrifuging, washed, and its weight and degree of polymerisation determined. The values of $[\eta]$ and the weight of substance extracted were used to construct a molecular weight distribution curve.

Bolotnikova and coworkers[108] used glycerol solutions as precipitants for the fractionation of cellulose from solutions in Cadoxene. It was shown that separation into molecular weight fractions takes place. Specimens of sulphite cellulose with $[\eta] = 4.9$ were separated into 8–10 fractions with $[\eta]$ from 6.1 to 2.2. To decrease the dwell time of the cellulose in the solution centrifuging was used to separate the fractions. In preliminary experiments on the reprecipitation of cellulose from solutions in Cadoxene it was shown that the destruction of cellulose during this is insignificant and $[\eta]$ varies by $\sim 9\%$.

Laamanen and Sihtola[109] used a 75% solution of propanol as precipitant for the fractionation of cellulose from solution in Cadoxene. This method was also employed by Kostnikova and coworkers[110], who showed agreement with the results of fractionation through the nitrates.

A paper recently appeared on the possibility of obtaining a molecular weight distribution curve for cellulose by gel chromatography on polyacrylamide gel[111]. The concentration of cellulose in the eluate was determined by Vasseur's method[112]. Specimens with degree of polymerisation 780, 1180, and 2000 were isolated as were two 50 : 50 mixtures of these specimens having degrees of polymerisation (DP) of 780 and 1180 and of 780 and 2000.

Various precipitants have been used for the fractional precipitation of cellulose from its solutions in the alkaline sodium tartratoferrate complex. Thus glycerol[53,113,114], water–methanol mixture (but up to 20% of the cellulose could

not be precipitated with this[115,116]), isopropyl alcohol[117], and glycol[117] have been used. Edel'man observed good agreement between distribution curves obtained in the fractionation of cellulose from solutions in STFC and by the nitrate method, when cellulose solutions taken for fractionation had concentrations ⩾ 0.2 g per 100 ml.

4. RELATION BETWEEN THE CHARACTERISTIC VISCOSITY AND MOLECULAR WEIGHT

The direct determination of the molecular weight of cellulose is hindered by the strongly acid and strongly alkaline nature of its solvents. The determination of molecular weight in solutions of complexes is complicated by the fact that in all the measurements (sedimentation, diffusion, light scattering) the kinetic species is a compound of cellulose with the complex, but as already mentioned there is no single opinion about the composition of the complex.

Gralen[118] determined the molecular weight of cellulose and its derivatives (xanthogenates and nitrates) using sedimentation and diffusion. Polydisperse specimens of cellulose were studied. The molecular weight was determined in the absence of air. Anomalies were observed in diffusion measurements on amminecopper solutions of cellulose but these were not noted for solutions of nitrates and xanthogenates. The diffusion process was retarded and began only after 2–3 days. Such an initial retardation of diffusion is explained[119] by the fact that some part of the copper is bound with the cellulose and diffuses together with it. The concentration of copper in the solution is less than that in the solvent. This also causes an apparent slowing of the diffusion owing to contradiffusion. In calculating the molecular weight Gralen started from Hess's ideas about the structure of the cellulose complex. Gralen gives his observations on the difference between the refractive index determined in sedimentation and diffusion measurements and with the aid of differential prisms. The author suggested that in the first instance the refractive index of the cellulosecopper compound changes, and in the second that of cellulose itself. The approximate conclusion was drawn that this difference corresponds to one atom of copper per glucose residue. From Gralen's results on molecular weight and characteristic viscosity in an amminecopper complex, Hermans[120] derived a relation between $[\eta]$ and molecular weight (M). This relation is shown in Table 1, Eqn. (4).

Michil[121] determined the molecular weight of cellulose from its nitrates when deriving the relation between characteristic viscosity and molecular weight of cellulose in solutions of the amminecopper complex. He calculated the molecular weight of the cellulose nitrate from the relation $[\eta] = f(M)$, determined by Hunt and coworkers[122] and by Holzer and coworkers[123] from results on light scattering. The molecular weights calculated from the relation obtained by Michil for amminecopper solutions of cellulose—Eqn. (5) in Table 1—agree well with the molecular weights measured by Gralen.

Table 1 also gives the relation between $[\eta]$ and M for amminecopper, Eqn. (6), and ethylenediaminecopper, Eqn. (8), solutions obtained by Marx[14]. The degree of polymerisation used in the derivation of these relations was determined from the viscosity of cellulose nitrates and calculated by the Schulz and Marx equation[124]:

$$[\eta]_g = 1.8 \cdot 10^{-3} P_w^{0.9} \text{ cm}^3 \text{ gf}^{-1},$$

where P_w is the weight-mean degree of polymerisation and $[\eta]_g$ was determined at a rate of 500 s^{-1}.

Immergut and coworkers[125] found a relation between characteristic viscosity and molecular weight for solutions of cellulose in amminecopper and ethylenediaminecopper complexes—Eqns. (7) and (9) in Table 1. Polydisperse specimens of cellulose with degrees of polymerisation from 100 to 3000 were investigated. The molecular weights of the cellulose were determined from measurements of the osmotic pressure in solutions of the corresponding cellulose nitrates (polydisperse and fractionated specimens). These investigators attempted to determine the molecular weight of celluloses (DP 408 and 166) in a solution of the ethylenediaminecopper complex with the aid of osmometry. Membranes of poly(vinylbutyral) and poly(chlorotrifluoroethylene) were used. The values of the number-mean molecular weights thus obtained agreed well with those calculated from the relations they obtained.

Table 1. Relation between characteristic viscosity and molecular weight for cellulose in various solvents.

Solvent	Specimens of Cellulose	Temp., °C	Relation $[\eta] = f(M)$, 100 ml g^{-1}			Method	Ref.
Amminecopper complex	polydisperse	25	$[\eta]=0.77\cdot10^{-2}$	$P^{0.81}$	(5)	NC_{ls}	121
	ditto	20	$[\eta]=85\cdot10^{-4}$	$M^{0.81}$	(7)	NC_{os}	125
ditto	"	20	$[\eta]=1.7\cdot10^{-4}$	$M^{0.77}$	(4)	sd	120
"	"	—	$[\eta]=6.8\cdot10^{-2}$	$P^{0.9}$	(6)	NC_{sd}	14
Ethylenediamine-copper complex	polydisperse	—	$[\eta]=9.8\cdot10^{-2}$	$P^{0.9}$	(8)	NC_{sd}	14
	ditto	25	$[\eta]=1.33\cdot10^{-4}$	$M^{0.9}$	(9)	NC_{os}	125
	"	25	$[\eta]=1.7\cdot10^{-2}$	$P^{0.8}$	(10)	os	126
Ditto	polydisperse	25	$[\eta]=1.7\cdot10^{-2}$	$P^{0.77}$	(12)	ls	27
"	hydrolysed	—	$[\eta]=1.8\cdot10^{-2}$	$P^{0.77}$	(13)	ls	27
Cadoxene		—	$[\eta]=2.5\cdot10^{-2}$	$P^{0.75}$	(11)	sd	27
"	polydisperse	20	$[\eta]=7.0\cdot10^{-3}$	$P^{0.9}$	(14)	NC_{sd}	127
"	fractionated	20	$[\eta]=5.93\cdot10^{-5}$	$M^{0.94}$	(15)	NC_{sd}	127
"	ditto	20	$[\eta]=9.33\cdot10^{-4}$	$M^{0.72}$	(16)	NC_{sd}	127
"	"	—	$[\eta]=3.85\cdot10^{-4}$	$M^{0.76}$	(17)	ls	130
Alkaline sodium tartratoferrate	polydisperse	25	$[\eta]=6.6\cdot10^{-3}$	$P^{1.01}$	(18)	sd	51
	"	—	$[\eta]=5.31\cdot10^{-4}$	$M^{0.78}$	(19)	ls	133

Note. The fifth column gives the method used for determining the molecular weight in the scaling relation $[\eta] = f(M)$: sd, sedimentation and diffusion; ls, light scattering; os, osmometry; NC, molecular weight determined viscosimetrically by conversion of the cellulose into cellulose nitrate; and the subscript shows by which method the relation $[\eta] = f(M)$ was found for cellulose nitrate.

Vink[126] found that solutions of cellulose in the ethylenediaminecopper complex can be diluted with water. Such solutions do not dissolve more cellulose but neither does precipitation of the cellulose take place. Therefore for determining the partial specific volume of cellulose Vink used dialysed solutions and converted the Svedberg formula for calculating the molecular weight of cellulose from sedimentation and diffusion measurements in such a way that the calculation gave the molecular weight not of the cellulosecopper complex (like Gralen), but of the cellulose itself:

$$M = \frac{RTS_x^0}{D_x^0 M_x / M\,(1 - \bar{V}_x \rho)},$$

where R is the universal gas constant, T the temperature, S_X^0 the sedimentation constant, and D_X^0 the diffusion constant

for the compound of the solvent with cellulose, extrapolated to infinite dilution, ρ the density, $\bar{V}_x$ the partial specific volume, M_x the molecular weight of the compound of cellulose with the solvent. Vink[126] determined the value of

$$\frac{M_x}{M}(1-\bar{V}_x\rho)$$

experimentally by dialysis of cellulose solutions of various concentrations. Anomalies in the diffusion experienced by Gralen[118] were avoided by Vink in the following manner. To prevent counterdiffusion of copper ion from the solvent to the solution he diluted the solvent with a little water. The molecular weights obtained by Vink were compared with those calculated by Marx' equation[14] and showed good agreement. Vink also determined the molecular weights by osmometry and found the relation between $[\eta]$ and M, Table 1, Eqn. (10).

Henley[27] used Vink's method when investigating solutions of cellulose in solutions of the ethylenediaminecadmium complex. The cellulose solutions were diluted with water in 1 : 1 ratio and contained alkali. Owing to the difficulty in obtaining fractions, Henley used polydisperse specimens obtained by acid hydrolysis of linters with polymerisation 5800. In such treatment a statistical molecular weight distribution with ratio $M_w : M_n = 2$ should be established, where M_w is the weight-mean and M_n the number-mean molecular weight. The relation between the molecular weight and $[\eta]$ obtained by Henley from the sedimentation and diffusion results are given in Table 1, Eqn. (11). Henley also determined the molecular weight of cellulose by a light scattering method. In studying the light scattering of solutions of cellulose in Cadoxene the increment in refractive index was determined after equilibrium dialysis at wavelengths of 5460 and 4358 Å; it was 0.183 and 0.186 ml g^{-1} respectively. The intensity of scattering was measured over the range of angles from 45° to 135°; the $[\eta] = f(M)$ relation—Table 1, Eqn. (12)—was found from the results on molecular weights and $[\eta]$.

Henley employed the usual Cellophane membranes in measuring the osmotic pressure of solutions of cellulose in Cadoxene diluted with water. Since it was assumed that $M_w : M_n = 2$, the values of M_w and M_n gave the viscosity-mean molecular weight and the relation $[\eta] = f(P_v)$, where P_v is the viscosity-mean degree of polymerisation, Table 1, Eqn. (13).

Bolotnikova and Samsonova[127] found the relation between $[\eta]$ and M for fractionated and polydisperse specimens of cellulose in solutions of the ethylenediaminecadmium complex not diluted with water. The molecular weights of cellulose were determined from the viscosity of their nitrates.

The molecular weight of the cellulose nitrates was determined by the relation:

$$[\eta] = 2.8 \cdot 10^{-5} M_{ww}^{1.00},$$

obtained by Meyerhoff[128,129] in investigating the sedimentation and diffusion of fractionated and polydisperse specimens of cellulose nitrate in acetone at 20°C. The molecular weights of several specimens of cellulose nitrate were determined by sedimentation and diffusion methods and their values agreed with those calculated by Meyerhoff's equation.

It was observed that there is a decrease in the slope of the relation between lg $[\eta]$ and lg M in the range of high molecular weights. Consequently this relation was found for two ranges of molecular weights. For fractionated specimens of cellulose with a molecular weight up to 400×10^3—that is, up to $[\eta] = 10$ g per 100 ml—the relation is described by the equation:

$$[\eta] = 5.93 \cdot 10^{-5} M^{0.94} \quad (100 \text{ ml g}^{-1}),$$

and in the range of molecular weights greater than 300×10^3 by

$$[\eta] = 9.33 \cdot 10^{-4} M^{0.73} \quad (100 \text{ ml g}^{-1}).$$

This difference in the values of the constants K and α in the Mark–Kuhn–Houwink equation $[\eta] = KM^{\alpha}$ between the low- and high-molecular weight ranges are due to the fact that at low degrees of polymerisation the final configuration of the coil has not been reached and the asymmetry of the molecules gradually decreases with increase in the molecular weight. Furthermore it can also be explained by the observed deterioration in the quality of the solvent for cellulose with a higher molecular weight. Brown and Wirkström[130] obtained similar results about the different nature of the relation between $[\eta]$ and M; they observed that at DP < 250 the conformation undergoes changes and the behaviour of the molecule departs from the behaviour of the coil. This agrees with the theories of the Kuhns, a verification of whose equations shows[131] that there is a change from the value $\alpha = 1$ in the range of low molecular weights to the value $\alpha = \frac{1}{2}$ in the range of high molecular weights, α being the exponent in the equation $[\eta] = KM^{\alpha}$. This change is due to a change in the trapping of the solvent in the coil of the chain molecule.

Vink[132] studied the behaviour of low-molecular-weight cellulose and oligosaccharides. For the oligosaccharides was determined in water, Cadoxene, and sulphuric acid. For degrees of polymerisation up to 150 a linear relation between $[\eta]$ and M was obtained. At lower degrees of polymerisation (< 100) the slope of the straight line $[\eta] = f(M)$ increases and consequently α also increase; the maximal value being $\alpha = 1.3$ at DP = 15. As has been shown[132], this behaviour of the molecules follows from their tendency to approach a prolate ellipsoidal form as the molecular weight is decreased.

Claesson and coworkers[51] made a diffusion and sedimentation investigation of solutions of cellulose in an alkaline solution of the sodium tartratoferrate complex which had been diluted with water; the relation between $[\eta]$ and M was obtained, Table 1, Eqn. (18). Later Valtasaari[133] obtained the $[\eta] = f(M)$ relation for solutions of cellulose in an alkaline solution of STFC by a light scattering method. This relation is also given in Table 1, Eqn. (19). Other relations between $[\eta]$ and M obtained by calculations from measurements of $[\eta]$ in two solvents, have been published[134].

5. DIMENSIONS AND FORM OF CELLULOSE MACROMOLECULES IN SOLUTION

Cellulose, like many synthetic polymers, is a linear unbranched polymer. However, the properties of cellulose solutions show a difference from those of flexible polymers, for example, those of the vinyl series. Thus it is well known that cellulose has a comparatively high characteristic viscosity ($[\eta]$), low sedimentation constant (S_0) and diffusion coefficient (D_0). Many of these properties, for example, $[\eta]$, are functions of the absolute dimensions of the macromolecules in the solution.

The dimensions and form of the cellulose macromolecules in solution are determined on the one hand by the size and structure of the monomeric unit, which is anhydro-*d*-glucose of cyclic structure, linked by a β-1,4-bond, and on

the other hand by the presence of three free hydroxyl groups, which determine the existence of both intra- and inter-molecular hydrogen bonds and also the specific nature of the interaction with the solvent.

To separate the influence of the solvent from the influence of the proper characteristics of the molecules, it is necessary to know the unperturbed dimensions in θ-conditions, that is, when the behaviour of the solution becomes ideal and the second virial coefficient equals zero.

The unperturbed dimensions depend on the size of the monomeric units, the lengths of the bonds between them, the valence angle, and steric and energetic hindrances to rotation around the intermonomeric bond. However, for cellulose it is experimentally difficult to attain the θ-condition, since the complexes in which cellulose is soluble exist in a narrow range of component concentrations and temperatures.

Samsonova and coworkers[135] calculated the unperturbed root mean square distances between the ends of the chain $\langle h_0^2\rangle^{1/2}$ for cellulose in Cadoxene by the Stockmayer–Fixman equation[136], by introducing the additional function $\Phi_0/\Phi(M)$[137]:

$$[\eta]\cdot\Phi_0/\Phi(M) = K_\theta M^{1/2} + 0.51B\Phi_0 M, \qquad (20)$$

where

$$K_\theta = \Phi_0\left(\frac{h_0^2}{M}\right)^{3/2}, \Phi_0$$

Φ_0 is the universal Flory constant equal to 2.86×10^{21} for a statistical gaussian coil, $\langle h_0^2\rangle^{1/2}$ is the unperturbed root mean square distance between the ends of the chain, M the molecular weight, B a parameter which characterises the polymer–solvent interaction and is proportional to the second virial coefficient, and $\Phi(M)$ is a function depending on the molecular weight introduced by Eizner and Ptitsyn[138] for the Flory constant with rigid macromolecules which are permeated by the solvent:

$$\Phi(M) = \frac{\Phi_0}{\left[\varphi(\lambda, n) + \frac{45}{32}\sqrt{\frac{2\pi}{3}}\frac{1}{3-\sqrt{2}}\frac{b_0}{r_0}\sqrt{\frac{\lambda}{n}}\right]\varkappa^{1/2}(n/\lambda)}. \qquad (21)$$

Here λ is the correlation length, equal to a/b_0, a the persistent length[139], b_0 the "dry" length of monomeric unit, found by an X-ray method to be 5.15 Å, and n is the degree of polymerisation.

It has been shown experimentally[27,140–143] for cellulose and its derivatives that Φ_0 depends on the molecular weight and only becomes constant at rather high molecular weights. This is explained by the great extension of the macromolecules in solution in the range of low molecular weights, so that gaussian statistics are attained only at high degrees of polymerisation when further interaction is small. It can be suggested that a change in Φ arises from the dependence of the permeability of these molecules on molecular weight.

Table 2 gives results on $\langle h_0^2\rangle^{1/2}$. Henley[27] calculated the unperturbed dimensions of cellulose macromolecules from the values of the Flory swelling coefficient α, which characterises the interaction of the polymer with the solvent and is equal to the ratio of the root mean square dimension of the disordered coil to the corresponding dimension of the unperturbed molecule

$$\alpha = \frac{\langle h^2\rangle^{1/2}}{\langle h_0^2\rangle^{1/2}},$$

and the value of $\langle h^2\rangle^{1/2}$ is the root mean square distance between the ends of the chain. The Henley swelling coefficient was calculated by the Orofino–Flory equation[144] from the experimental results for the second virial coefficient determined by the light scattering method and from the root mean square radius of gyration of the chain $(\bar{R}^2)^{1/2}$.

Table 2. Dimensions of the macromolecules of cellulose and its derivatives calculated by Eizner and Ptitsyn's theory[138].

System	$[\eta]$	n	λ	$\langle h^2\rangle^{1/2}$	$\langle h_0^2\rangle^{1/2}$	$h_{max}/\langle h^2\rangle^{1/2}$	α
Cellulose in Cadoxene	6.20	2100	13	1100	840	9.1	1.4
	5.50	1730		1000	760	8.3	
	4.50	1260		900	650	6.9	
Solution of cellulose in Cadoxene diluted with water, 1:1 (Ref.27)	6.45	2090	13	1000*	837	10.8	1.4
	5.50	1700		855*	754	10.2	
	4.47	1300		735*	660	9.1	
Cellulose nitrate in acetone	24.1	2940	46	2600	1700	5.8	1.4
	14.7	1800		2100	1300	4.4	
	10.7	1300		1740	1130	3.8	
Ethyl cellulose in ethyl acetate	1.87	331	13	412	260	3.5	1.5
	1.40	246		350	225	3.1	

* The values given are for $\langle h^2\rangle_W^{1/2}$ calculated from $\langle h^2\rangle_Z^{1/2}$ obtained from results on light scattering[27].

Table 3. Dimensions of macromolecules in solutions of cellulose and its derivatives.

System	$[\eta]^{25°}$, dl g^{-1}	n_w	$(R^2)_z^{1/2}$	$\langle h^2\rangle_z^{1/2}$	$\langle h_0^2\rangle^{1/2}$	$\langle h_0^2\rangle^{1/2}/\langle h^2\rangle_f^{1/2}$	α	Ref.
Solution of cellulose in Cadoxene diluted with water, 1:1	14.15	5820	895	2190	1780	2.47	1.23	27
	6.45	2290	585	1430	1300	2.86	1.10	
	5.50	1780	485	1190	1050	2.62	1.13	
	4.47	1400	445	1090	1010	2 87	1.08	
Hydroxyethyl cellulose in water	10.62	2650	750	1830	1690	3.6*	1.08	141
	10.00	2420	730	1790	1670		1.07	
	8.95	2180	715	1750	1650		1.06	
	1.70	340	305	745	715		1.04	
Hydroxyethyl cellulose in Cadoxene	6.30	2560	620	1520	1070	2.3*	1.42	141
	6.00	2420	600	1470	1140		1.29	
	5.55	2230	575	1405	1020		1.38	
	1.24	330	255	625	575		1.09	
Sodium carboxymethyl-cellulose in Cadoxene	10.30	4420	835	2040	1400	2.3*	1.46	140
	8.10	3500	735	1800	1280		1.41	
	4.84	2000	550	1350	1040		1.29	
	2.55	1800	330	810	660		1.22	

* The values are approximate, since in calculating $\langle h_0^2\rangle^{1/2}$ the Stockmayer–Fixman theory was used, which cannot be employed in the investigated ranges of molecular weight for cellulose and its derivatives[148].

The value of $(\bar{R}^2)$ is the mean square of the distances r_i of all the elements of mass (atoms) of the chain from its centre of inertia[145];

$$(\bar{R}^2) = \frac{1}{N}\sum r_i^2,$$

where N is the number of units in the molecule. At sufficiently high molecular weights, when a gaussian distribution inside the macromolecule has been reached, statistical theory leads to the following relation:

$$(\bar{R}^2)^{1/2} = \frac{1}{6}h^2.$$

Henley[27] determined $(\bar{R}^2)^{1/2}$ experimentally for solutions of cellulose in Cadoxene diluted with water from the slope of the scattering relation at zero concentration (Table 3) and calculated it from values of S_0, D_0, $[\eta]$, and M. However,

good agreement between the calculated and experimentally determined values was not obtained, except for the calculation of $(\overline{R^2})^{1/2}$ from $[\eta]$ and M. Samsonova and coworkers[135] calculated the mean square distance between the ends of the chain according to the Eizner and Ptitsyn theory[138], in which the rigidity and finite length of the chain are allowed for by introducing two functions $\varphi(\lambda,n)$ and $\kappa(n/\lambda)$; $\kappa(n/\lambda)$ takes into account the factor of chain rigidity and the function $\varphi(\lambda,n)$ allows for possible departures from gaussian statistics at low degrees of polymerisation.

Information about the sizes of cellulose macromolecules of various molecular weights is given in Tables 2 and 3, which also gives for comparison the dimensions of cellulose derivatives in various solvents[27,135,140-143]. It also gives values of the swelling coefficient α, which takes into account the contribution of the effect of the interaction of the polymer with the solvent. It was found that the dimensions of the macromolecules of cellulose and its derivatives in solution are appreciably greater than those of synthetic polymers at the same degree of polymerisation. The greater dimensions of the macromolecules of cellulose and its derivatives are due firstly to the greater size of the monomeric units $b_0 = 5.15$ Å (for polystyrene $b_0 = 2.54$ Å), and secondly to the greater elongation of the macromolecules owing to restricted rotation around the C–O bond between monomer units. This was shown for both cellulose[27] and its derivatives[140-143,146] by a comparison of $\langle h_0^2\rangle^{1/2}$ calculated from the experimental results with the values of $\langle h^2\rangle_f^{1/2}$ calculated assuming free rotation around the bond between monomer units. It was found that $\langle h_0^2\rangle_f^{1/2}$ is 2–3 times greater than $\langle h_0^2\rangle_f^{1/2}$ (Tables 3–6) and the ratio $\langle h_0^2\rangle^{1/2}/\langle h^2\rangle_f^{1/2}$ increases with decrease in molecular weight, showing the change in the elongation of the macromolecule with M. Furthermore, the restriction of rotation around the intermonomeric bond is shown by the high values of cos Φ[27,140-143] which is a parameter of steric hindrance. At sufficiently high values of n an analysis of hindrances to rotation can be made by using the equation:

$$h_0^2 = Nb_0^2\left(\frac{1-\cos\theta}{1+\cos\theta}\,\frac{1+\cos\Phi}{1-\cos\Phi}\right), \qquad (22)$$

where N is the total number of units, θ the oxygen valence angle in cellulose and its derivatives (~ 110°), and Φ the angle between the planes of successive bonds. When rotation around the C–O bond is unrestricted, cos $\Phi = 0$, and in the absence of free rotation with maximal elongation cos $\Phi = 1$. For cellulose cos $\Phi = 0.78$,[27] that is, the steric hindrances in the cellulose chain should be one of the factors which determine the form of the cellulose molecules in the solution. For amylose cos $\Phi = 0.81$[147] and for hydroxyethyl cellulose[143] cos $\Phi = 0.89$. In the last instance the high value of cos Φ is due to the presence of additional hindrances, owing to the hydroxyethyl side-groups having approximately the same length as the monomeric unit b_0.

Table 5. Comparison of A_m and b for cellulose and its derivatives.

System	A_m, Å	b, Å	Method	Reference
Solution of cellulose in Cadoxene diluted with water (1:1)	54	24	sd	27
	147	23	visc.	
	107	23	ls.	
Cellulose in Cadoxene	100	25	visc.	135
Hydroxyethylcellulose in water	51	23	sd.	143
	182	27	visc.	143
	176	30	ls.	143
	180	30	ls.	141
Hydroxyethylcellulose in Cadoxene	124	25	ls.	141
Ethyl hydroxyethylcellulose in water	120	—	sd	154
	216	37	visc.	154
Methyl cellulose in water	87	—	sd	27
Ethyl cellulose in ethyl acetate	100	23	visc.	135
Cellulose nitrate in ethyl acetate	234	35	ls.	122

Table 4 gives the dimensions of the macromolecules of various polysaccharides calculated by the Eizner–Ptitsyn theory[128,135,137,149-153]. On comparing the results given in Tables 2–4 we see that the dimensions of almost all the polysaccharides, except cellulose nitrate and hydroxyethyl cellulose in water, are approximately the same at the same degrees of polymerisation, as is shown by the almost equal values for the correlation lengths λ and for the persistent length a. This shows that polysaccharides having a β-1-4

Table 4. Dimensions of the macromolecules of various polysaccharides calculated by the Eizner–Ptitsyn theory.

No.	Polymer	Solvent	M_0	Range of $[\eta]$, dl g^{-1}	Range of SP	λ	a	$(R^2)^{1/2}$, Å	Reference
1	birch xylan	90% DMSO	149	0.24—0.88	55—194	6.6	34.2	48—102	149
2	Canadian spruce xylan	alkali borates	137	0.37—0.57	174—406	2.7	14.2	69—102	150
3	cellulose acetates	trifluoroethanol	249	0.46—1.11	46—136	11.0	55.6	49—101	150
4	cellulose acetate	acetone	249	0.27—2.30	33—377	11.5	59.3	39—190	150
5	cellulose acetate	acetone	260	1.23—5.05	190—1000	14.7	75	150—375	137
6	cellulose	Cadoxene	162	1.47—14.15	1390—5830	13.8	70.8	405—839	27
7	cellulose	STFC	162	2.85—15.15	385—3950	13.8	71.9	206—695	133
8	cellulose trinitrate	acetone	294	0.36—15.30	44—2142	25.5	132	56—684	128
9	cellulose xanthogenate diethylacetamide	90% DMSO	238—336*	1.79—2.67	473—1190	10.5	54.0	203—378	151
10	cellulose caproate	dioxan	459	0.32—3.80	86—3160	9.3	47.7	72—514	150
11	galactomannan triacetate	acetonitrile	432	0.44—9.45	171—1236	11.2	57.8	118—1106	152
12	glucomannan triacetate	nitroethane	288	2.28—6.25	1130—4080	10.7	55.3	323—620	150
13	polystyrene	benzene	52.1	0.27—0.90	433—2260	13.2	20.4	64—153	153
14	"	cyclohexane	52.1	0.18—0.40	433—2260	6.0	9.8	44—103	153

bond, and also an α-1-6 bond in the example of galactomannates, have the same configuration, which is almost independent of the lateral substituent groups.

The small differences in λ, for example, for acetylcellulose ($\lambda = 11-14.7$) can be explained by the difference in the degrees of polymerisation, since with increase in n the effect of excluded volume begins to be apparent. An especially pronounced dependence of λ on DP was observed for cellulose nitrate[135]. The lower rigidity of pentosans compared with hexosans can be explained by the fact that xylan, which has five carbon atoms has greater free rotation around the ether bond than hexosans. True, at the low value of $\lambda = 6.6$ xylan can have too low a DP. The value of $\lambda = 2.7$ for xylan from canadian spruce is thought to be erroneous by the investigators themselves[150], probably owing to errors in the molecular weight determination by the light scattering method, where the effect of lignin impurities and of the aggregation of the particles should appear.

Table 6. Parameters which characterise the undisturbed state for cellulose and its derivatives in Cadoxene and polystyrene in toluene.

Polymer	b, Å	A_m, Å	A_m, mol. units	$(h_0^2)^{1/2}/(h^2)^{1/2}_f$	Reference
Cellulose	19	70	14	2.7	27
Hydroxyethylcellulose	18	62	12	2.4	141
Sodium carboxyethylcellulose	18	60	12	2.4	140
Polystyrene in toluene	8.6	33	13	2.2	156, 157

The comparatively low value of λ for cellulose caproate is explained by the fact that it was obtained under θ-conditions.

The other values given in Tables 2 and 5, show the degree of elongation or the flexibility of the macromolecules. The relation $h_{max}/\langle h^2\rangle^{1/2}$ characterises the degree of convolution of the macromolecules, where h_{max} is the contour length of the completely extended molecule $= nb_0$. $A_m = h^2/h_{max}$ is the effective length of the Kuhn statistical segment, which is a measure of the short-range interactions affecting the length of the segment and characterising the chain "rigidity". Here the "rigidity" of the chain signifies the elongation owing to restricted rotation around the intermonomeric bond rather than resistance to deformation. $b = (h^2/n)^{1/2}$ is the effective length of the monomeric unit just as the persistent length a [139] is a measure of the "rigidity" of the chain.

A comparison of these quantities shows that cellulose has the same degree of convolution, or the inverse quantity, degree of elongation, as its derivatives, with the exception of cellulose nitrate and of hydroxyethyl cellulose in water. The great extension of the macromolecules of cellulose nitrate is due to the presence of the strongly polar NO_2 groups, and that of hydroxyethyl cellulose in water to the presence of intramolecular hydrogen bonds, which have a considerable effect on free rotation around the intermonomeric bond. Here solutions of hydroxyethyl cellulose in water are very stable; they can be heated to boiling or large quantities of precipitant (salts or dimethyl sulphoxide) can be added without precipitation of the polymer—a difference from methyl cellulose[154]. The addition of precipitant has no effect on the change in the molecular elongation of the hydroxyethyl cellulose. This independence of the composition of the solvent can be explained by the presence of intramolecular hydrogen bonds, which play a large part in the form of the macromolecules in solution. An increase in the hydrophobic nature of the substituents in ethylhydroxyethylcellulose leads to less extension, and an increase in the degree of substitution in methyl cellulose (28% methoxy-groups) to a more compact structure.

For sodium carboxymethylcellulose the dimensions and form of its macromolecules in solution depend on the ionic strength of the solvent. At a high ionic strength (in Cadoxene and 1 N NaCl) the CMC molecule behaves like cellulose and other uncharged derivatives of cellulose in Cadoxene and has the same dimensions. It is less extended than hydroxyethyl cellulose in water. With decrease in the ionic strength the dimensions of the coil increase considerably, by approximately a factor of 2 (for a change in ionic strength from 0.2 M NaCl to 0.005 M NaCl) owing to interaction between the charged groups.

The great dimensions of the macromolecules of cellulose and of derivatives in real, that is, non-ideal, solutions is due to the considerable spreading of the molecules due to interaction with the solvent, which has been characterised[27,135,140-143] by the swelling coefficient α, which is the effective excluded volume. Here the nature of the interaction with Cadoxene is the same for both cellulose and those derivatives which are soluble in the solvent.

The swelling coefficient is rather high (1.4) but less than the values given in the tables for specimens with low n, which suggests that a gaussian distribution of the segments inside the coil is not achieved. The low value of α for hydroxyethyl cellulose in water again suggests a more elongated form for the macromolecules.

Water has a great affinity for the hydroxyl groups and forms a compact solvate layer around the macromolecule which decreases with increase in temperature.

The size of the cellulose macromolecules in Cadoxene is also affected by the fact that Cadoxene does not simply solvate the cellulose but forms a more stable compound with it than the solvates. The existence of a compound of cellulose with the solvent the electronic polarisability of which is sufficiently high suggests a high value for the increment in refractive index dn/dc which is approximately 0.18 for cellulose in Cadoxene[27] and in sodium tartratoferrate complex[52].

The second virial coefficient for cellulose[27] and its derivatives in Cadoxene[140-143] is rather high ($A_2 = 10-17 \times 10^{-4}$) which suggests good interaction of the polymer with the solvent. Since the presence of hydrogen bonds in cellulose requires very polar solvents for its dissolution, it is natural that after the cellulose has dissolved these solvents become "good" in the thermodynamic sense in relation to the cellulose macromolecules. An analysis of the thermodynamic parameters for the interaction of the polymer with the solvent showed that cellulose and its derivatives have a negative entropy of mixing[142,155], which shows the compact arrangement of the solvent molecules around the polymer segments. The nature of the interaction of cellulose and its derivatives with the solvent depends on the degree of polymerisation, the temperature, the degree of substitution (in the cellulose derivatives) and also the nature of the solvent.

The strongly negative temperature coefficient of the characteristic viscosity for cellulose and its derivatives shows a decrease in the elongation of the macromolecules with increase in temperature, which is mostly connected with the weakening of the polymer–solvent bond. This is

also shown by the change in α with temperature. Furthermore, the values of α and A_2 depend on the degree of polymerisation[27,140-143,146].

On comparing the unperturbed dimensions of cellulose and its derivatives with polystyrene we see that the flexibility of cellulose in solution is not very different from the flexibility of polystyrene, the number of monomeric units in the equivalent Kuhn statistical segment is almost the same but a greater degree of polymerisation for cellulose and its derivatives is needed only to achieve the conformation of a statistical coil.

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Institute of High-molecular-weight
Compounds, Academy of Sciences
of the USSR, Leningrad