A new solvent for cellulose

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A new solvent for cellulose was prepared by dissolving copper (II) hydroxide in an aqueous solution of 1,3-diaminopropane. The solvent displays an efficiency equal to cuprammonium and superior to other previously reported metal complex solvents; a mechanism for the dissolution has been proposed. Solutions of cellulose in the new solvent were used to prepare thin cellulose membranes.

Introduction

For many purposes naturally occurring cellulose is dissolved in a suitable solvent and regenerated in some desired form: fibres, films and, more recently, hollow fibres. Known cellulose solvents have been reviewed[1] but only two processes have some commercial importance. The viscose process dominates the industry and has largely replaced the cuprammonium process developed in the 19th century. However, films and hollow fibres manufactured from cuprammonium are still considered to be the best material available for use in artificial kidney machines[2].

We were interested in the mechanism of cellulose dissolution in cuprammonium and other metal complex solvents, and the relationship between method of preparation and the properties of regenerated films[3]. Our work in this area led to the discovery of a new, very effective cellulose solvent from which we have prepared cellulose films.

The known cellulose solvents[1,4] related to cuprammonium have certain features in common: all contain a kinetically labile metal ion held in a weakly alkaline solution by ligands which may be displaced fairly easily (ammonia and 1,2-diaminoethane have been used). It is generally accepted that cellulose solution occurs by a ligand displacement reaction, the glucose units in the cellulose chain replacing some but not all of the ligands in the metal ion's coordination sphere. More specifically some deprotonation of the hydroxyl groups must occur (hence the alkaline solution) and the C-2 and C-3 hydroxyl groups chelate to the metal ion[5]. Electron paramagnetic resonance spectra[6] support the idea of a strong chemical bond between these hydroxyls and copper atoms in Cu/NH_3 (cuprammonium) and Cu/en (copper(II) hydroxide dissolved in an aqueous solution of 1,2-diaminoethane).

Experimental

Preparation of Cu/pn solvent. Copper(II) sulphate-5-water (25 g) was dissolved in water (200 cm³) and 2M sodium hydroxide (110 cm³) was added with stirring. The precipitate of copper(II) hydroxide was filtered at the pump and washed with water; as much water as possible was removed by suction. The moist copper(II) hydroxide was suspended in water (325 cm³) and 1,3-diaminopropane (25 cm³) was added dropwise with stirring. The deep blue solution was filtered through a glass wool plug.

In some preparations the volume of water used to suspend the copper(II) hydroxide was less; this gave a more concentrated solvent which was then diluted to give a range of concentrations.

Preparation of saturated cellulose solutions. Filter paper (Whatman number 1) was weighed, cut into small pieces and pulped in distilled water using a food blender. The pulped solid was filtered at the pump, added to 100 cm³ of solvent and the mixture stirred mechanically for 1 hour. The amount of filter paper used was determined by the solvent concentration; in each case a 10–20% excess of cellulose over that required for a 1:1 glucose unit to copper(II) ion ratio was taken.

In some of our earlier work cotton wool was used rather than filter paper; this was not pulped prior to dissolution.

Analysis of solutions. Undissolved cellulose was removed by centrifuging. At high copper concentrations a non-running deep blue gel formed and this was diluted with a known amount of water before centrifuging. The diluted solutions were stable enough to allow centrifuging and subsequent analysis but cellulose precipitated slowly from then upon standing.

Cellulose was regenerated from a weighed sample of solution with dilute sulphuric acid. It was filtered, washed thoroughly with distilled water and dried to constant weight at 60°C. The copper content of the filtrate was determined iodiometrically.

Preparation of cellulose films. A 2% w/w solution of cellulose in Cu/pn was poured onto a glass plate (45 cm × 30 cm). A stainless steel bar, with tape at each end to provide a 0.45 mm gap, was used to spread the solution over the plate. The spread solution was placed in a bath containing 3 mol dm⁻³ sodium hydroxide solution for 5 min. It was transferred to a water bath and, after 5 min, placed in a bath containing 2 mol dm⁻³ hydrochloric acid for 8 min. The reformed cellulose film was left in running water for a minimum of 30 min after which it was clamped in a wooden frame and allowed to dry in a constant humidity cabinet (approximately 65% relative humidity).

Results and Discussion

Using available data[4] we have calculated the 'efficiencies' of known metal complex solvents (*Table 1*). We define efficiency as the number of glucose units per metal ion in the most concentrated cellulose solution that has been prepared from the solvent in question. The most efficient solvent is cuprammonium, where a ratio of one glucose unit to each copper(II) ion is found. Other workers[7,8] have suggested a 1:1 ratio of glucose units to copper(II) ions in the soluble cellulose species found in cuprammonium solutions. We believe that this is the ratio of glucose units to metal ions for the soluble species in all solvents, but that an excess of the metal ion must be present in the less efficient solvents. Solvents based on ammonia contain a large excess of the ligand while just sufficient 1,2-diaminoethane to dissolve the metal hydroxide or oxide is used.

In view of the suggested dissolution mechanism the stability of the metal complex used as the solvent is important. Basing our new solvent on copper (since Cu/NH_3 and Cu/en are very efficient, and cuprammonium is an industrially used solvent) we decided to use 1,3-diaminopropane (pn) as the ligand. Six-membered chelate rings containing copper(II) and a neutral bidentate ligand are less stable than related 5-membered rings; this is illustrated by the following aqueous equilibrium[9]:

$$(Cu\,en_2)^{2+} + 2pn = (Cu\,pn_2)^{2+} + 2en; \quad K = 1.38 \times 10^{-3}$$
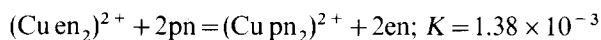
It seemed probable, therefore, that a solution of copper(II) hydroxide in aqueous 1,3-diaminopropane (Cu/pn) would be an effective solvent for cellulose and this was clearly demonstrated. The solvent undoubtedly contains a mixture of ions in dynamic equilibrium but the predominate species is probably $[Cu(NH_2CH_2 CH_2CH_2NH_2)_2(H_2O)_2]^{2+}$, which may be presented as $(Cu\,pn_2)^{2+}$.

Pulped filter paper and cotton wool dissolved very readily in the new solvent, Cu/pn. The solutions were very viscous, much more so than cellulose solutions of similar concentration in Cu/NH_3. Furthermore the solutions appeared quite resistant to oxidative degradation, remaining viscous over storage times of several days. The Analytical data for saturated cellulose solutions in Cu/pn (*Table 2*) show that the solvent has an efficiency (as defined earlier) equal to Cu/NH_3 and superior to all previously reported metal complex solvents. A 1:1 ratio of glucose units to copper(II) ions was found when the copper concentration of the cellulose solution exceeded 0.015 moles per 100 g solution. The lower efficiencies observed at low copper concentrations suggest an equilibrium between $(Cu\,pn_2)^{2+}$ ions and the species in solution with cellulose complexed to the copper(II) ions.

It was not possible to obtain cellulose solutions of higher concentrations because they would have been too viscous to handle. It may be feasible to produce such solutions by using cellulose of a lower average relative molecular mass.

The ligand exchange mechanism for cellulose dissolution in metal complex solvents is well accepted. We would like to endorse the argument with the following comments:

(a) The new solvent, Cu/pn, is more efficient than Cu/en as anticipated; the complex of lower stability dissolves

Table 1 'Efficiences' of known metal complex solvents

Solvent	Glucose units per metal ion at maximum cellulose concentration	
Cu/NH_3	0.96	
Ni/en	0.68	
Cu/en	0.52	
Ni/NH_3	0.49	decreasing
Cd/en	0.47	'efficiency'
Co(II)/en	0.36	
Zn/en	0.27	
Co(III)/en	no dissolution	

Table 2 Analyses of saturated cellulose solutions in Cu/pn (all concentrations in moles/100 g solution)

Copper concentration	Glucose unit concentration*	Glucose : copper ratio
0.00362	0.00038	1 : 0.10
0.00688	0.00330	1 : 0.48
0.00709	0.00461	1 : 0.65
0.0141	0.0121	1 : 0.86
0.0141	0.0130	1 : 0.92
0.0168	0.0181	1 : 1.08
0.0174	0.0180	1 : 1.03
0.0198	0.0196	1 : 0.99
0.0231	0.0225	1 : 0.97

* Calculated by assuming all cellulose to be composed of glucose units of relative molecular mass 162

cellulose more efficiently in terms of glucose units per copper(II) ion in solution.

(b) Oxidation of Co(II)/en solvent gives a non-cellulose dissolving solution of Co(III)/en[4]. In retrospect it can be noted that cobalt(II) compounds are kinetically labile but cobalt(III) compounds are kinetically inert. Further, no chromium(III) complexes have been reported to dissolve cellulose; chromium(III) is also kinetically inert.

(c) When 2-aminoethanol is used as the ligand in conjunction with copper(II) the resulting blue solution does not dissolve cellulose[3]. This is probably because 2-aminoethanol deprotonates when reacting with copper(II) hydroxide and the resulting complex[10] is too stable to exchange with cellulose. Furthermore, the solution would contain very few free hydroxide ions.

(d) At least partial deprotonation of the glucose units in the cellulose chain must occur. Cellulose only dissolves if the solution is alkaline and, indeed, dissolution in cuprammonium is enhanced by the addition of small amounts of alkali metal hydroxides[11].

We suggest that cellulose dissolves in Cu/pn according to the reaction shown in *Figure 1*. For each glucose unit in the cellulose chain the C–2 or C–3 hydroxyl group deprotonates and the glucose unit displaces one of the co-ordinated 1,3-diaminopropane molecules. Further deprotonation is not envisaged; rather it is thought that this occurs in the alkali treatment during regeneration of the cellulose as a thin film. The reaction with excess alkali releases some copper(II) ions and the remaining blue solid is found to contain two glucose units for each copper(II) ion and no 1,3-diaminopropane[12].

Clear, colourless cellulose films were regenerated from solutions of cellulose in Cu/pn. When the solution, supported on a glass plate, was placed in the alkali bath a clear, blue, solid sheet formed which often floated free of the glass. The alkali became deep blue and it was evident that a reaction had occurred. Excess alkali was removed
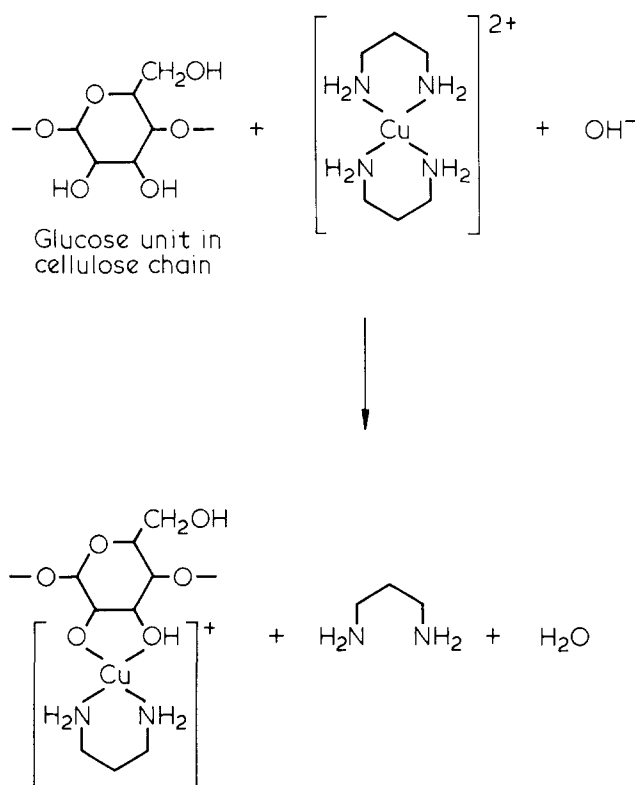
Figure 1 Proposed mechanism for the dissolution of cellulose in the new solvent (the axial coordination positions of copper have been omitted; these are probably occupied by water molecules)

by immersing the blue solid in a water bath, and the cellulose reformed as a thin film by transferring the supported material to a bath containing dilute hydrochloric acid. It was important to wash the regenerated films thoroughly; inadequate washing led to dried films which were rather yellow (presumably due to contamination with copper(II) chloride) and which crumbled when touched. Well-washed films appeared to be similar in strength to Cu/NH_3 films prepared under the same conditions. The dialysis properties of Cu/pn films are now being studied and compared with Cu/NH_3 films in our laboratories.

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