Supplementary Material (ESI) for Green Chemistry

Cationic functionalisation of cellulose using a choline based ionic liquid analogue

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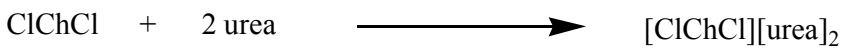
Supplementary Information:

[ClChCl][urea]$_2$ deep eutectic solvent



General procedure for eutectic solvent formation[1]
Chlorcholine chloride (ClChCl) (12.96 g, 0.082 mol) was added to urea (9.78 g, 0.163 mol) and the mixture heated to 80°C and stirred occasionally for 30 minutes. A clear viscous liquid was formed and the ionic liquid was cooled to room temperature. The liquid can be kept at room temperature for at least 1 month as long as it is adequately protected from moisture using parafilm.

Cationic functionalisation of cellulose (general procedure)

Cellulose (in the form of cotton wool; 0.1 g, 3.10 x 10^{-4} mol) was added to the [ClChCl][urea]$_2$ deep eutectic solvent (5 ml) followed by sodium hydroxide (0.372 g, 9.30 x 10^{-3} mol). The mixture was heated with stirring at 90°C for 15 hours before being allowed to cool. The cotton wool was extracted from the eutectic solvent and washed copiously with water.

Dye calibration plot

Different concentrations of methylene blue dye solution were made up and the UV absorbance determined by UV/Vis spectroscopy – Table 1

Table 1 UV absorbance values of different concentrations of dye solution.

Entry	Concentration/ moldm^{-3}	UV absorbance
1	9.89 x 10^{-6}	0.946
2	7.42 x 10^{-6}	0.725
3	4.95 x 10^{-6}	0.495
4	3.47 x 10^{-6}	0.343
5	1.98 x 10^{-6}	0.201
6	1.48 x 10^{-6}	0.156
7	9.89 x 10^{-7}	0.130

The calibration plot produced from this data is shown below (Figure 1).

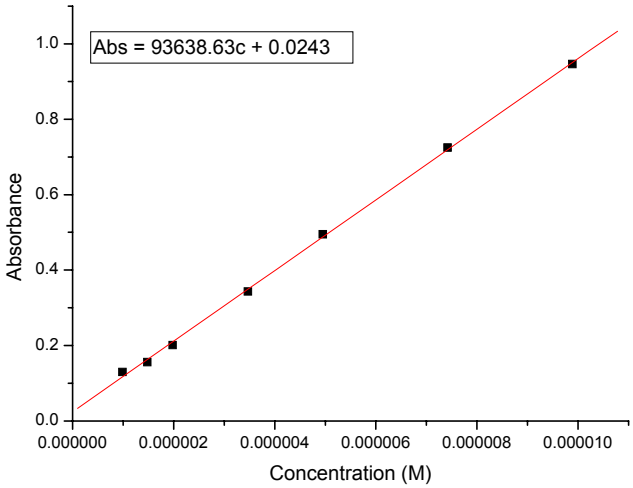
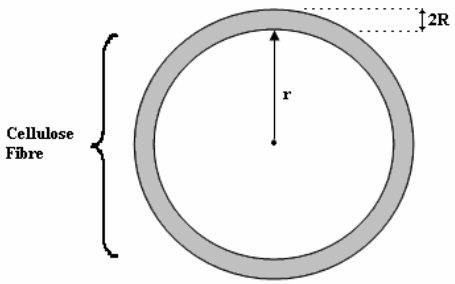


Figure 1 Calibration plot relating concentration (c) of dye solution with UV absorbance (Abs)

Estimation of ratio of surface hydroxyl groups to those in the bulk of the monomer

The percentage ratio of hydroxyl groups on the surface to those in the bulk material was estimated using a model based on the simple geometry of a cellulose fibre (Figure 2).



where:
r = radius of the cellulose fibre
R = radius of the glucose monomer on the surface of the fibre

Figure 2 Representation of cellulose fibre (not to scale)

And from this an equation generated:

Ratio of surface hydroxyl groups to those in the bulk of the monomer: $\frac{\pi(r + 2R)^2 - \pi r^2}{\pi(r + 2R)^2}$

References:

1. A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, V. Tambyrajah, *Chem. Commun.*, 2003, 70.