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Perichromism: A powerful tool for probing the properties of cellulose and its derivatives

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ABSTRACT

This overview is concerned with the use of certain dyes (perichromic indicators, hereafter designated as “probes”) in order to determine the properties of cellulose, its solutions and solid derivatives. It is arranged as follows: (i) the properties of cellulose and its derivatives that are relevant to their applications are listed; (ii) a general discussion is presented on how perichromism can be employed in order to gain information on the medium where the probe is present; (iii) the results of perichromism, as applied to cellulose, cellulose solutions, and derivative films are discussed.

1. Relevant properties of cellulose and its derivatives

The semi-crystalline nature of cellulose fibers bears on their useful mechanical properties and determines their accessibility; hence reactivity in any intended application, dyeing, derivatization, etc. In general terms, the accessibility of cellulose depends on its origin, processing condition, and composition, i.e., index of crystallinity (I_c), degree of polymerization (DP), and contents of α-cellulose, hemicellulose, and lignin.

Derivatization of cellulose leads to modifications of several physico-chemical properties that are relevant to processing of the derivatives obtained, in particular, extrusion as fibers, slabs, dyeing; adsorption, etc. The reason is that derivatization leads to the substitution of a strongly dipolar group that acts as hydrogen-bond donor and acceptor, OH, with less dipolar groups that act as hydrogen-bond acceptors, e.g., acyl or ether group. Therefore, cellulose–substrate interactions that are driven by hydrogen-bonding and dipolar interactions, e.g., adsorption of dyes and proteins will be affected (Edgar, 2007; Inglesby & Zeronian, 1996, 2002). The dependence of the properties of cellulose carboxylic acid esters on the degree of substitution (DS) is readily reflected, e.g., in their glass transition-, melting-, and decomposition temperature (Fidale et al., 2010); optical properties (Necula, Olaru, Olaru, Homocianu, & Ioan, 2010); solubility in organic solvents (Carollo, 2004; Rustemeyer, 2004). Regarding cellulose ethers, in particular, carboxymethyl cellulose (CMC) the viscosity and the effects of electrolytes on the stability of its aqueous solutions are sensitively dependent on the DS. CMC is applied in diverse fields, ranging from the pharmaceutical and food industries to the muds employed in petroleum drilling (Heinze & Koschella, 2005). Another important example is the dependence of the hydrophilic/hydrophobic character on DS. Various cellulose derivatives, including esters (Diamantoglou, Lemke, & Vienken, 1994), ethers (Toufik, Carreno, Josefowicz, & Labarre, 1995), and other derivatives (Diamantoglou, Platz, & Vienken, 1999) are promising materials for hemodialysis membranes, because of their blood compatibility.

As stated above, it becomes clear that the properties, hence applications of cellulose derivatives depend on the corresponding DS, the regularity of substitution within the anhydroglucose unit (AGU) and along the biopolymer backbone (El Seoud & Heinze, 2005). This dependence can be readily rationalized: the derivatization of cellulose corresponds to a gradual substitution of a dipolar group (e.g., ester, tosylate) or an ionic group ($-CH_2CO_2Na$; CMC) for the strongly dipolar OH group of the AGU. Based on this, it is clear that the interactions of cellulose and its derivatives with any medium, liquid or solid, will be the sum of specific- (e.g., acid/base interactions; electrostatic interactions) and non-specific interactions (van der Waals).

Therefore, knowledge of the effects of cellulose derivatization on these (specific and non-specific) interactions is necessary for a series of applications, e.g., films and fibers applied in separation and reverse osmosis (Kesting, Ditter, Jackson, & Murray, 1979; Matsuura & Sourirajan, 1972); dyeing (Stana-Kleinschek, Strnad, &

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Ribitsch, 1999; Zollinger, 1991); gas sorption (Puleo, Paul, & Kelley, 1989); nano-composites (Moura, Lorevice, Mattoso, & Zucolotto, 2011); optical properties (Greiner et al., 2003); miscibility with other polymers, and chemical reactivity in further derivatization reactions (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998); reinforcement of polymer matrixes (Israelachvili, 1991), etc. The ensuing discussion answers the following question: can these interactions be determined, and their relative contribution quantified?

2. Perichromism: fundamentals and applications

A brief description of the origin of the phenomenon and the terms employed is presented. In principle, the spectrum of any substance, absorption or emission, is expected to be affected by the (surrounding) medium. What distinguishes perichromic probes from other substances, e.g., aliphatic alcohols, chlorinated hydrocarbons, simple aromatics, etc., is that the (ground state → excited state) transition energy is highly medium-sensitive. The perichromic probes usually show medium-dependent colors; hence the "chrom" part of the term. Perichromism describes the effect of any medium on the color of a probe; the term solvatochromism is employed for liquids (solvents and their mixtures, aqueous micelles). Therefore these two terms will be employed interchangeably, depending on the physical state of the medium.

There have been several approaches to quantify the dependence of chemical phenomena on solvent properties, most notably the simplified Taft–Kamlet–Abboud equation, where the (redundant) cavity term is disregarded (Abraham, Grellier, Abboud, Doherty, & Taft, 1988; Kamlet, Abboud, & Taft, 1981; Laurence, Nicolet, Dalati, Abboud, & Notario, 1994). A medium dependent phenomenon (MDP), e.g., a spectroscopic shift, a rate constant, etc., is modeled as a linear combination of two hydrogen-bonding terms, in which the medium acts as a hydrogen-bond donor ($a\alpha$), or hydrogen-bond acceptor ($b\beta$), and a dipolarity/polarizability term [$s(\pi^* + d\delta)$]; ($d\delta$) is a correction for π^*. An approach has been advanced in order to separate the dipolarity from polarizability (Catalán, 2009).

$$\text{MDP} = \text{Constant} + a\,\alpha + b\,\alpha + s(\pi^* + d\delta) \qquad (1)$$

The parameters (α), (β), and (π^*) are known as perichromic parameters because they are determined using perichromic probes (vide infra). The information sought about the medium is derived as follows: from the spectra of the probe, an empirical polarity scale, E_T(probe) is calculated from Eq. (2) (El Seoud, 2007, 2009):

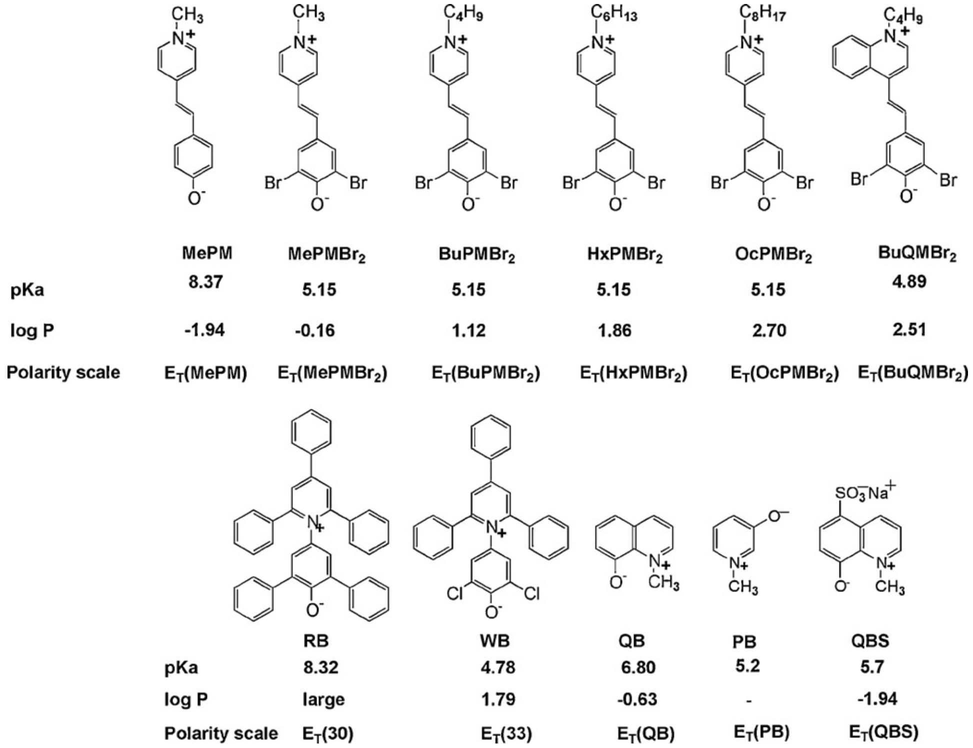
$$E_{\mathbf{T}}(\text{probe}),\quad \text{kcal/mol} = \frac{28591.5}{\lambda_{\max}}(\text{nm}) \qquad (2)$$

This equation converts the electronic transition within the probe into the corresponding intra-molecular charge-transfer energy. Values of E_T(probe) are then rationalized in terms of non-specific and specific probe-solvent interaction mechanisms (Martins, Lima, & El Seoud, 2006).

$$E_{\mathbf{T}}(\text{probe}) = \text{Constant} + a\,\alpha + b\,\beta + s(\pi^* + d\delta) + p\ \ \log P \qquad (3)$$

where a new term ($p \log P$) has been introduced because the spectroscopic response of merocyanine probes is sensitive to solvent lipophilicity, as measured by the empirical scale $\log P$ (= partition coefficient of a substance between (mutually saturated) 1-octanol and water: $\log P = \log([\text{substance}]_{\text{1-octanol}}/[\text{substance}]_{\text{water}})$). Fig. 1 shows some solvatochromic probes that the group of one of the authors has employed in order to study solvents, and their binary mixtures, along with their pK_a in water and $\log P$.

As an example of the determination of the relative importance of probe–medium (liquid or solid) interaction mechanisms, consider the solvation of perichromic probes. The procedure in order to extract this information is as follows: we determine the effects of a group of solvents on the UV–vis spectra of one or more probes; we apply Eq. (2) in order to calculate E_T(probe); we use Eq. (3) in order to calculate the regression coefficients (a), (b), (s), and (p). Finally, we draw conclusions about the relative importance of



	MePM	MePMBr$_2$	BuPMBr$_2$	HxPMBr$_2$	OcPMBr$_2$	BuQMBr$_2$
pKa	8.37	5.15	5.15	5.15	5.15	4.89
log P	-1.94	-0.16	1.12	1.86	2.70	2.51
Polarity scale	E_T(MePM)	E_T(MePMBr$_2$)	E_T(BuPMBr$_2$)	E_T(HxPMBr$_2$)	E_T(OcPMBr$_2$)	E_T(BuQMBr$_2$)

	RB	WB	QB	PB	QBS
pKa	8.32	4.78	6.80	5.2	5.7
log P	large	1.79	-0.63	-	-1.94
Polarity scale	E_T(30)	E_T(33)	E_T(QB)	E_T(PB)	E_T(QBS)

Fig. 1. Molecular structures of zwitterionic perichromic indicators, employed for determining medium empirical polarity. Along with the pK_a of their conjugate acids in water; and $\log P$. The acronyms of the probes and the corresponding empirical polarity scales are also indicated.

medium acidity, basicity, etc., from these regression coefficients, after their values have been *statistically standardized.* Values of (α), (β), etc. are known for a myriad of substances (liquids and solids). Where not available, they can be determined by using appropriate perichromic indicators. Because these probes are sensitive, *to varying extents*, to more than one solvent property, the information required is obtained by manipulating the spectra of pairs of homomorphs. These are molecules that have the same, or closely related structures, e.g., 4-nitroaniline and *N*,*N*-dimethyl-4-nitroaniline for the calculation of β. In this pair, the latter is sensitive to dipolar interactions and can only act a base, by accepting a hydrogen-bond from the substrate (e.g., the OH of the AGU). The former is sensitive to the same interactions, in addition to acting as acid/base. Manipulation of $\lambda_{\max}$ of both probes in a series of media permits cancelation of the effect of all medium–probe interactions on perichromism, *except medium basicity*, this allows calculation of β (Lagalante, Spadi, & Bruno, 2000).

In principle, therefore, it should be possible to determine important properties of cellulose or its derivatives by use of perichromic probes. Of these, surface acidity, basicity, and dipolarity/polarizability are most relevant. For example, determination of these as a function of DS shows how the conversion (Cellulose-OH → Cellulose-substituent) affects the properties of the interface, hence the forces acting therein.

3. Application of perichromism to cellulose and its derivatives

Using perichromic probes in order to investigate the surface properties of cellulose derivatives offers several advantages. The method is simple, fast, reproducible, and requires easily accessible apparatus such as a spectrophotometer with a reflectance attachment. Care should be taken, however, because the method is sensitive to the presence of impurities, whose perichromic parameters are different from those of cellulose, or cellulose derivative. Potentially, these include residual impurities and sub-products carried over from the synthesis; water sorption during manipulation of the sample. The source of an additional error is the deposition of several layers of the indicator on the film surface. In extreme cases, the probe in the upper layer is sampling the next probe layer, and not the film surface. These problems are eliminated by using carefully purified samples and by running control experiments, as detailed elsewhere (Fidale et al., 2010). Of particular importance here is that cellulose esters hydrolyze detectably in the solid phase over time to liberate carboxylic acid. As expected, the reaction is autocatalytic. Therefore, they should be purified, e.g., by repeated washing with warm ethanol, drying, and keeping in a refrigerator.

Several probes have been employed in order to investigate the surface properties of cellulose and their derivatives. Fig. 2 shows the molecular structures of some of these probes. Reichardt's dye, 2,6-diphenyl-4-(2,4,6-triphenyl-pyridinium-1-yl)phenolate, RB does not adsorb sufficiently on cellulose fibers; it is easily protonated on the phenolate oxygen due to its high pK_a (Fischer & Spange, 2000; Spange, Zimmermann, & Grässer, 1999), e.g., by carboxylic acid liberated due to cellulose ester hydrolysis during storage. This, if it occurs, suppresses the intra-molecular ($O^- \rightarrow N^+$) charge transfer, leading to loss of the perichromic band. This is an important reason for purifying the sample employed. As shown in Fig. 1, there are many perichromic probes whose pK_a values are ca. 5, i.e., are less prone to this protonation.

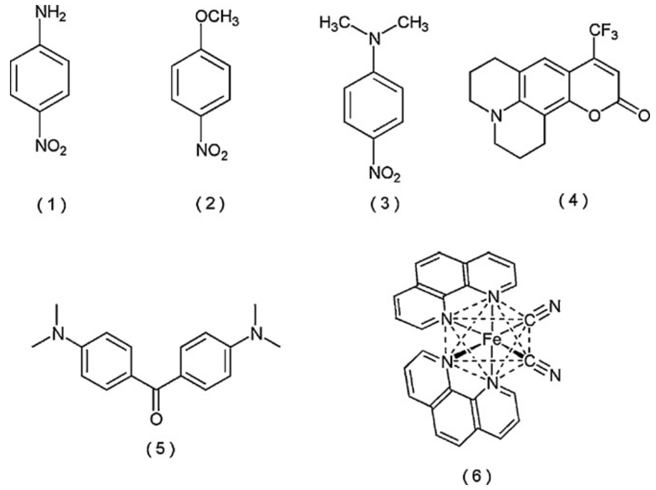


Fig. 2. The molecular structures of some perichromic probes that have been employed for the study of cellulose, its solutions, and derivatives. Probes 1, 2, 3, 4, 5, and 6 refer to 4-nitroaniline; 4-nitroanisole; 4-nitro-*N*,*N*-dimethylaniline; coumarine 153; 4,4′-bis(*N*,*N*-dimethylaminobenzophenone); *cis*-dicyano-bis(1,10-phenanthroline)-iron, respectively.

As an example of the flexibility that perchromism offers, consider the probe WB. Its perichromism has been studied in pure solvents; binary solvent mixtures (El Seoud, 2007, 2009), and solid surfaces (El Seoud, Ramadan, & Sato, 2010; Khristenko, Kholin, Mchedlov-Petrossyan, Reichardt, & Zaitsev, 2006). Although the presence of two ortho chlorine atoms in the phenolate moiety lowers its pK_a (in water = 4.78), this does not decrease its hydrogen-bonding ability, relative to (extensively employed) RB (Tada, Novaki, & El Seoud, 2000). Additionally, WB is not very hydrophobic, therefore, it is unlikely to auto-aggregate in solution, or at a solid surface, or to be protonated by traces of acid impurities present in the sample. The fact that the $E_T(30)$ scale is much more extensive than its $E_T(33)$ counterpart poses no practical problem because both scales are inter-convertible by using the linear correlation (Tada et al., 2000): $E_T(30) = 0.979\, E_T(33) - 7.461$ ($n = 32$ protic and aprotic solvents, linear correlation coefficient, $r = 0.9905$).

4. Cellulose and its solutions in non-derivatizing solvents

The properties of native and regenerated celluloses have been investigated. Values of $E_T(30)$ can be calculated either directly or (where RB does not adsorb properly on the sample) using the perichromic parameters (α) and (π^*) (Marcus, 1993): $E_T(30) = 31.2 + 15.2\,\alpha + 11.5\,\pi^*$ ($n = 155$, linear correlation coefficient, $r = 0.98$) (Bigos, 2000; Spange et al., 1998). The experimentally determined $E_T(30)$ values (51.4–53.0 kcal/mol), were found to be lower than those calculated from other perichromic parameters, 54.7–57.7 kcal/mol, for native celluloses samples (linter, microcrystalline, sulfite kraft-pulp, prehydrolyzed kraft-pulp, bacteria cellulose) (Fischer, Spange, Bellmann, Adams, & Fischer, 2002; Spange, Fischer, Prause, & Heinze, 2003). Additionally, the empirical polarities of native celluloses from different origins cannot be classified in terms of relatively well defined ranges, as is usual for the different classes of protic and aprotic solvents. The (π^*) term, however, serves as a suitable parameter for classifying the surface polarity of different native cellulose batches. The values of (α) show a wide distribution in the amorphous sections and a narrow distribution in the crystalline part of cellulose. Both the strength and the concentration of hydrogen bond donor, HBD surface groups contribute to (α). Therefore, this is a specific parameter that varies significantly due to the pre-treatment of the cellulose, and basicity of the probe employed. In summary, the perichromic method maybe akin to a finger print for detecting small differences in the surface properties of various cellulose batches.

The effect of accessibility of the hydroxyl groups of the AGUs on surface properties has been demonstrated. Thus, steam explosion converts (less accessible) hydroxyls of banana fiber into (more accessible) hydroxyls in the resulting fibrils. The latter material was bleached; parts were subjected to chemical modifications, by treatment with benzoyl chloride; $KMnO_4$, or vinyl trimethoxy silane. The surface properties have been investigated by employing dyes 5, 6 (Fig. 2) and 3-(4-amino-3-methylphenyl)-7-phenyl-2,6 dihydrofuran; [2′,3′:4,5] benzofuran-2,6-dione (Paul et al., 2008). The authors observed an increase of (α) from 1.56 to 1.84 for banana fibers and fibrils, respectively. Steam explosion followed by bleaching results in cellulose with an increased degree of crystallinity and crystallites of larger size (Focher, Marzetti, Beltrame, & Avella, 1998). The combined effect of these structural changes contributes to the increase in (α). Banana fibrils also shows higher π^* value (0.58), as compared with that of the corresponding fiber (0.38). The $E_T(30)$ parameter increases after steam explosion followed by bleaching, from 59.2 to 63.0 kcal/mol, and (β) increased from 0.43 to 0.73, for banana fibers and fibrils, respectively (Paul et al., 2008).

5. Cellulose solutions in non-derivatizing solvents

Derivatization of cellulose under homogeneous solution conditions has several advantages, in particular, control of the average DS, and the distribution pattern among the AGUs, and along the polymer chain (El Seoud & Heinze, 2005; Hudson & Cuculo, 1980). Solvatochromic parameters can be used as a tool in order to investigate the relative importance to dissolution of solute–solvent interaction mechanisms (Spange, Keutel, and Simon, 1992; Spange et al., 1998). Spange et al. have employed probes number 5, 6 of Fig. 2, WB, and copper(II)-*N*,*N*,*N*′,*N*′-tetramethylethylendiamine-acetylacetonate (Cu(tmen)(acac)) in order to investigate the properties of cellulose proper; the solvent *N*,*N*-dimethylacetamide, DMA–LiCl; and cellulose/DMA–LiCl solutions. The influence of the electrolyte concentration on the solvatochromic properties of DMA–LiCl was studied. The values of (α) increased from 0 to 0.6, on increasing [LiCl] from 0% to 15%. Because the acidity of unsolvated Li^+ is high (Marcus, 1991), the lower values obtained for DMA/LiCl indicate a strong complexation of Li^+, forming $Li^+(DMA)_n$ macrocations. The $E_T(30)$ and (β) values were affected drastically with increasing the concentration of LiCl. The (β) value obtained for LiCl/DMA (7.5%) was 2.0. This is the highest basicity ever reported for chloride ions, or hydrogen-bond accepting solvents. The authors showed that the dissolution of cellulose in this solvent system has no influence on $E_T(30)$, the values for the DMA/LiCl, and cellulose/DMA/LiCl solution, were the same, 53 kcal/mol. The (β) data indicated that the chloride–cellulose interactions contributes about 80% to the dipolar–dipolar interactions between DMA and cellulose, whereas the specific $Li/(DMA)_n$-cellulose interactions contribute about 10%. These results agree with previous conclusions on the mechanism of cellulose dissolution in DMA/LiCl (El-Kafrawy, 1982; El Seoud & Heinze, 2005; McCormick & Lichatowich, 1979).

Ionic liquids (IL) have been employed as solvents for cellulose dissolution/derivatization. Frequently, cellulose solutions in IL are highly viscous; some are immiscible with non-polar reagents, or reaction products (El Seoud, Koschella, Fidale, Dorn, & Heinze, 2007). The addition of molecular solvents to cellulose/IL can minimize these problems, provided that their addition does not lead to cellulose precipitation. This requires an understanding of the role of the molecular co-solvent, and its interactions with cellulose, and the IL. The effects of 18 molecular solvents and 3 binary solvent mixtures on cellulose solutions in three ILs, 1-allyl-3-methylimidazoliumchloride, 1-butyl-3-methylimidazolium chloride, and 1-ethyl-3-methylimidazolium acetate, have been recently studied with respect to the solution phase behavior. The best results were obtained using molecular solvents with relatively high empirical polarity and basicity, and relatively low acidity (Gericke, Liebert, El Seoud, & Heinze, 2011).

Table 1
Correlations of perichromic parameters for cellulose esters, CAs, CBs, and CHs.[a]

Entry	Sample	Probes[a]	Plot equations	*n*	*r*
1	CA	WB	$E_T(33) = 69.153 - 4.234\ \mathrm{DS}$	20	−0.9985
2	CA	3 (Fig. 2)	$\pi^* = 1.219 - 0.113\ \mathrm{DS}$	9	−0.9983
3	CA		$\alpha = 0.363 + 0.894\, e^{(-\mathrm{DS}/0.563)}$	9	0.9950
4	CA		$\beta = 0.339 + 0.618\, e^{(-\mathrm{DS}/1.019)}$	9	0.9915
5	CB	WB	$E_T(33) = 65.169 - 4.0\ \mathrm{DS}_{CB}$	8	0.997
6	CH	WB	$E_T(33) = 62.861 + 4.006\ \mathrm{DS}_{CH}$	9	0.996

[a] Data taken from Casarano et al. (2011).

6. Cellulose derivatives

The surface properties of some cellulose derivatives have been studied by perichromic probes, including: cellulose acetates (CAs), Spange, Heinze, and Klemm (1992) butyrates (CBs) and hexanoates (CHs); carboxymethyl celluloses (CMCs); cellulose tosylates (CTs), and others derivatives (Casarano, Fidale, Lucheti, Heinze, & El Seoud, 2011; Fidale et al., 2010; Fischer, Heinze, & Spange, 2003; Spange et al., 2003).

The perichromism properties of cellulose tosylates (CTs), DS from 0.38 to 1.68 were investigated (Fischer et al., 2003). The dependence of $E_T(30)$ on DS gave unsatisfactory correlation; the values of (α) decreased, whereas those of (π^*) increased as a function of increasing DS (Eqs. (4) and (5)), the latter result is due to an increase of surface polarizability due to the introduction of aromatic moieties.

$$\mathrm{DS_{CT}} = 3.64 - 3.489\,\alpha \quad n = 8 \quad r = 0.763 \tag{4}$$

$$\mathrm{DS_{CT}} = -1.695 + 3.419\,\pi^* \quad n = 8 \quad r = 0.763 \tag{5}$$

Recently, the *systematic dependence* of the perichromism properties of CAs (acidity, basicity, dipolarity/polarizability) on the DS has been investigated (Fidale et al., 2010). Nine CAs samples, DS from 0.83 to 3.0 were synthesized; and their films were prepared and analyzed, using probes 1, 2, 3, and WB (Fig. 2). The dependence of perichromic parameters of CA on DS can be described by simple equations; linear for $E_T(33)$ and π^*; exponential decay for (α) and (β) (Table 1, entries 1–4). The change, linear or not, of the perichromic property as a function of increasing DS is a consequence of the substitution of the strongly dipolar OH groups that acts both as hydrogen bond acceptor and donor, by the weakly dipolar acetate moiety that act as hydrogen bond acceptor. Likewise, the empirical polarities $E_T(33)$ of CBs, and CHs have been determined for DS from 0.7 to 2.7 (Casarano et al., 2011). As shown in Fig. 3 and entries 5 and 6 of Table 1, all plots are linear, and almost parallel, with excellent correlation coefficients. The intercepts decrease as a

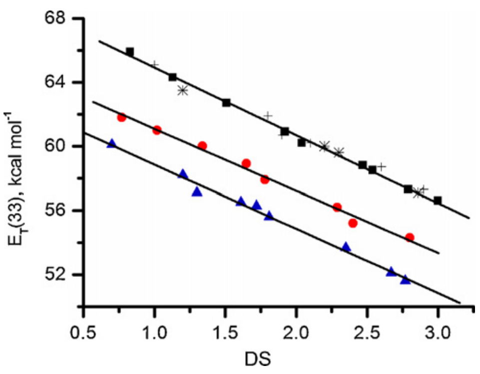


Fig. 3. Dependence of $E_T(33)$ on DS of cellulose esters. The points shown are for CAs obtained from the acetylation of MCC in LiCl/DMAc (*), or in IL (+); from the acetylation of fibrous celluloses in LiCl/DMAc (■); for CBs (●); for CHs (▲). The latter two esters were obtained by acylation of MCC in IL.

Reproduced from Casarano et al. (2011).

Table 2
Correlations between perichromic parameters and DS for CMCs.[a]

Entry	Plot equations	n	r
1	$DS = 2.20 - 1.462\,\alpha$	11	0.733
2	$DS = 3.561 - 0.067\,AN$	11	0.903
3	$E_T(33) = 51.639 + 1.743\,DS$	10	0.9945
4	$\pi^* = 1.191 + 0.119\,DS$	7	0.9970
5	$\beta = 0.160 - 0.030\,DS + 0.027\,DS^2$	7	0.9977

[a] Data from Fischer et al. (2003) and Fidale et al. (2011).

function of increasing the number of carbon atoms, N_C, of the acyl moiety.

The first perichromic study of the properties of CMC, DS from 0.48 to 1.96, was carried out by Fischer et al. (2003). Probes 5, 6 (Fig. 2) and 4-aminobenzophenone were employed for the determination of surface properties. The values of (α) and AN (Gutmann's acceptor number) were found to decrease with increasing DS, entries 1 and 2 of Table 2. However, the corresponding $E_T(30)$, (β), and (π^*) showed no clear dependence on DS. Recently, the properties of films of CMC, DS in the range 1.13–2.43, were determined by the use of perichromic probes, 1, 2, 3, and WB (Fig. 2). The correlations between $E_T(33)$- or (π^*) and DS were found to be linear; that between (β) and DS is a second order polynomial with high correlation coefficient (entries 3, 4 and 5, respectively); no obvious correlation was found between DS and (α).

Concerning others cellulose derivatives, there is no information on the effects of variation of DS on the properties. Table 3 show the perichromic parameters of hydroxyethyl- (HEC), hydroxypropyl- (HPC), methylhydroxyethyl- (MHEC), sulfoethyl- (SEC), methylcellulose (MC) dicarboxymethylcelluloses (DCMC) with different DS. These results have been determined using the probes 5, 6 (Fig. 2) and 4-aminobenzophenone (Fischer et al., 2003).

7. Applications of dye perichromism: an expedient and accurate method for the determination of DS of cellulose derivatives

As discussed in the preceding section, there are excellent correlations between the perichromic properties and DS. Consequently, we have suggested that this method can be fruitfully employed for the determination of DS of cellulose derivatives, including cellulose esters, CAs, CBs, and CHs and cellulose ether, CMCs (Casarano et al., 2011). The excellent linear correlations shown in Fig. 3 for CAs is satisfying for several reasons: the high correlation coefficient observed; the results are *independent* of the experimental variables, including the type of cellulose (microcrystalline, cotton, eucalyptus, and sisal), and the solvent employed in the synthesis (DMA/LiCl, or IL). The results are independent of structure and lipophilicity of the probe employed, WB or $MePMBr_2$ (Fig. 2). Fig. 4 shows that the dependence of $E_T(33)$ on DS of CMCs is linear for commercial samples as well as those synthesized in the laboratory.

Table 3
Perichromic parameters of cellulose derivatives.

Sample	DS	α	β	π^*	AN	$E_T(30)$ (kcal/mol)
HEC	0.73	0.64	0.31	0.74	33.17	49.46
HEC	1.62	0.66	0.46	0.82	34.02	50.72
HPC	0.73	0.66	0.28	0.61	33.60	48.29
HPC	1.54	0.68	0.41	0.93	34.87	52.21
MHEC	1.52a	0.62	0.52	0.64	32.34	47.91
SEC	0.42	0.94	0.79	0.88	42.54	55.52
SEC	0.91	0.81	0.75	1.00	38.95	55.01
MC	0.90	0.63	0.56	0.68	32.75	48.56
MC	1.75	0.54	0.41	0.61	29.86	46.37
DCMC	0.89	0.82	0.91	0.50	38.34	49.45
DCMC	1.73	0.78	0.85	0.55	37.02	49.32

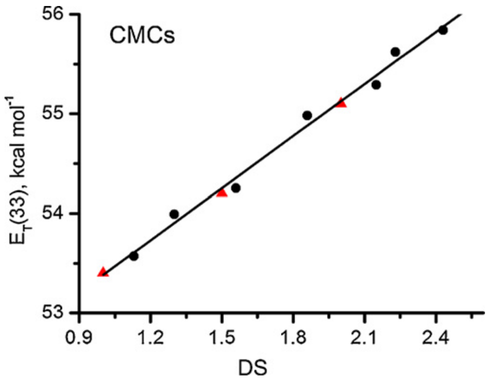


Fig. 4. Dependence of $E_T(33)$ on DS of CMCs. The points shown are for CMCs synthesized (●), or commercial fibrous samples (▲).

Data reproduced from Casarano et al. (2011) and Fidale et al. (2011).

8. Conclusions

There is a need to understand, on the molecular level, the properties of different celluloses, their derivatives, and solutions in non-derivatizing solvents. Perichromism is a simple and powerful tool to do the job; it offers information on the overall polarity, as well as the acidity, basicity, and dipolarity/polarizability. This approach is attractive because of the availability of a large number of probes; the simplicity of the equipment; and the relatively straightforward correlation between the perichromic response and the property sought. Further investigation, however, is still needed on the effects of *systematic* structural variation of cellulose derivatives on the properties of their films. For example, Tables 1 and 3 show that only few derivatives have been examined so far by this technique. It is important to determine, e.g., the surface properties of mixed esters because of the relevance of their blood compatibility, vide supra.

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