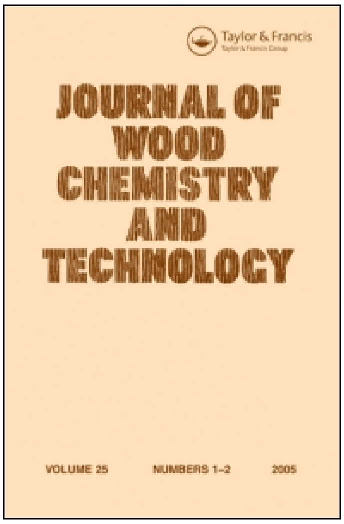

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Applications of Electrometric Techniques in Wood Chemistry

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APPLICATIONS OF ELECTROMETRIC TECHNIQUES IN WOOD CHEMISTRY

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ABSTRACT

A review is given of the application and limitations of potentiometric and potentiostatic (polarographic and voltammetric) studies. Quantitative determinations of pulp-relevant systems (liquors) and compounds (sulfur and lignin compounds; quinoid and non-quinoid additives) at ambient and mid-range temperature (90 ± 10°C) as well as under soda pulping conditions are described. A specially developed pressure cell for the elucidation of the fate and mechanism of additives at temperatures up to 150°C is presented.

INTRODUCTION

Since the introduction of the potentiometric method permitting a rapid and direct determination of the Na_2S-content of sulfate black liquor without interference from organic sulfides and other substances usually present by Borlew and Pascoe[1] in 1946, and the first publication in 1957 by Enkvist[2] on experiments concerning the role of the redox potentials and hemicellulose during sulfate cellulose digestion, a growing interest in the application of electrochemical methods - primarily potentiometric ones - and in recent years of polarographic

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and voltammetric methods is to be noticed in pulping chemistry.

The sensitivity, accuracy and application aspects of polarographic and voltammetric techniques are some of the stimulating facts for the increased application of these techniques for the study of reduction and oxidation potentials, the solubility and stability of wood components and additives, but also for the elucidation of the additive behavior and fate in connection with delignification and carbohydrate stabilization under pulping conditions.

In this paper the state of the art is briefly reviewed of

(I). The application of electrometric methods to the analysis of relevant compounds in pulp chemistry such as liquors and additives. (The application of polarography to the study of lignin and lignin models has long been recognized and practised in Russia).

(II). The application of potentiometric techniques to the determination of redox potentials of liquors.

(III). The polarographic and voltammetric study of pulping additives at ambient, 90°C and in situ at 150°C during pulping. Voltammetric measurements made at 150°C under pulping conditions were presented for the first time at the Ekman-Days[6] meeting.

(I). ELECTROANALYSIS OF RELEVANT COMPOUNDS IN WOOD CHEMISTRY: SULFUR COMPOUNDS: LIGNIN AND LIGNIN MODELS: QUINOID AND NON-QUINOID COMPOUNDS

(I.1) Electroanalysis of Sulfur Compounds in Delignification Chemistry

The most successful methods for selectively and quantitatively measuring sulfide, sulfite, thiosulfite and sulfhydryl compounds in kraft black liquors have been electrochemical[7]. Potentiometric methods were reported as early as 1946 by Borlew and Pascoe[1]. (For a review of the analysis of black liquor up to 1961, see Yorston[8]).

Potentiometric methods using commercially available ion-selective electrodes proposed in the last decade involve the use of a sulfide-ion-selective electrode either for direct potentiometric determinations[9,10] or as an end-point indicator for titrations with mercuric salts[9,10,11,12]. These techniques were reported to be the best available methods in 1975[13]. An indirect method uses a Cd-ion-selective electrode (determination of the Cd-ion excess after precipitation of the sulfides by $Cd(NO_3)_2$))[14,15].

The ion-selective electrode is also used for the determination of sodium in black liquor[21].

For the continuous monitoring in situ at 170°C of the free sulfide ion-concentration during a kraft pulping process a probe consisting of two ion-selective electrodes was developed by Renaud et al[22,23].

The apparent unreliability of potentiometric determinations of sulfides in black liquor[12,15] (instability of sulfide ions towards oxidation[14,16]) led Renard, Kubes and Bolker[13] to introduce polarography.

Ac-[13], dc-[17], and pulse-[7,18] polarography were proposed for the determination of sulfide, polysulfide, mercaptan, thiosulfate and sulfite in white and black liquors.

Differential pulse polarography is said to be especially well suited for the analysis of oxidized black liquor which normally contains a low concentration of sulfides and a relatively high concentration of thiosulfate[7].

The determination of mixtures of sulfides, thiosulfate and sulfite is certainly more straightforward by polarography than by either potentiometric or volumetric methods and can be used for the control of any step in the recovery of kraft pulping chemicals and in studies dealing with the kinetics of kraft pulping and oxidation of black liquors[13]. Cernak et al [18,19] proposed square wave polarography for the computer control of the sulfate process, which needs an accurate analysis of the sulfate delignification liquor at a given moment in addition to other data[19,20].

(I.2) Voltammetric/Polarographic Studies and Voltammetric Determination of Lignin and Lignin Model Compounds

Korytseva and Vodsinskii[24] have proposed a rapid, reliable and precise method for the determination of residual lignin in cellulose pulp and in pine, spruce, birch, beech and aspen by measuring the oxidation current on a stationary pyrographite working electrode in water/DMF (9:1)Na_2HPO_4-supporting electrolyte. Using the same voltammetric technique they determined lignin and lignosulfonates in purified waste waters from pulp and paper plants and in natural reservoirs.

Voltammetric analysis is said to be more accurate - the detection limit of lignin is 1 mg/l - than the colorimetric one[25]. The voltammetric oxidation of lignins at a graphite electrode was studied in detail by Korytseva and co-workers[26,27]. Under the given experimental conditions no oxidation wave was found at a Pt-electrode[28,29,30] unlike with various phenol related lignin model compounds. Evstigneev et al in their analysis of the lignin functional composition studied the reduction of 17 lignin model compounds using dc-and ac-polarography[31].

Ac-polarographic studies of spruce wood lignin revealed 6 peaks in $DMSO/Bu_4NClO_4$ over a wide range of potentials; 5 of which are ascribed to the reduction of carbonyl groups and one is considered to be a tensammetric peak[32]. Björkman lignin and dioxane lignin produce 5 and 7 peaks, resp. the number of peaks depending on the isolation procedure of the lignin. The reduction of lignin model compounds was studied in aprotic medium[33] as well as in aqueous LiOH[34] (on this point see also Peter et al[35]).

Electro-oxidation of dissolved organics at a carbon fiber electrode is the basis of a process recommended for treatment of kraft mill effluents[39].

(I.3) Analysis of Quinoid and Non-Quinoid Compounds in Pulp-Relevant Matrices

Considering the number of papers on anthraquinone (AQ) and non-quinoid additives published in the past 3-4 years, only a small number of analytical papers has appeared.

For process research studies using anthraquinone (AQ), good analytical techniques are needed to determine AQ and its reduced forms as well as addition products of AQ and lignin and of AQ and carbohydrates.

It is now becoming clear that the side reactions which remove AQ from the catalytic pulping cycle take place via reduction products of AQ (anthranol, anthrone, anthracene; 9,10-dihydroanthracene[36]) and not via AQ itself.

Many of the by-products formed from AQ during alkaline pulping share the robust nature of the parent molecule for example the highly stable benzanthrone[37]. Benzanthrone-, anthrone derivatives are polarographically active though their polarographic determination in liquors has not been reported so far.

The major reduction product of AQ is 9,10-anthracenediol (AQH_2)[36,38]. The formation of AQH_2 can be detected by polarography and voltammetry (see chapter III.2.3) and by the appearance of a red color in the pulping liquor.

Minor quantities of anthrone, anthracene and 9,10-dihydroanthracene were also observed by GC-MS[36] in a variety of matrices such as black liquor, pulp, plant air and waste water[40] . Hrutfiord[41] in 1979 found most of the additive in the black liquor and only trace amounts in the pulp[42]. Anthrone has been found in soda-AQ-black liquors obtained from spruce cooks. Although anthrone yield was too small to be detected by the polarographic technique used, it may be detected by HPLC[40].

Recent studies have shown that of the AQ applied initially in alkaline pulping, only a relatively small proportion is recoverable at the end of the cook, so supporting the conclusion that AQ combines chemically with lignin and carbohydrate fragments[37]. Cooking studies carried out with sawdust of _Fagus sylvatica_ and _Picea abies_ in the presence of NaOH and C^{14} - labelled AQ e.g. showed that 5.2 to 11.8 % of the activity is present in the resulting pulp[42]. For the study of the fate of anthraquinone in soda pulping, Algar et al[43] cooked _P.elliottii_ chips with sodium hydroxide and C^{14}-AQ and measured the activity of various black liquor fractions at different stages of pulping.

In 1981, Armentrout[40] published the liquid chromatographic determination of AQ in soda and kraft pulping liquor, pulp, air filters and waste water. Mortimer and Fleming[44,45] described the chromatographic determination of AQ in pulping liquors. With HPLC 1 - 400 mg AQ/l were determined in acetonitrile extracts of soda-AQ and kraft-AQ-pulping liquors. The HPLC method is also applicable to pulp extracts, tall oil and tall oil soaps that contain AQ. Harruff[46] developed a simple GC method with electron capture detection for analysis of AQ in pulp toluene extracts. Further methods for determining AQ in pulping black liquor involve either exhaustive chloroform extraction followed by GC-MS (see e.g.48) or oxidative ac-polarographic measurements of 9,10-anthracenediol (AQH_2) after reduction of AQ to AQH_2 with sodium dithionite[38]. According to Brønstad et al[47] the polarographic method used by Fleming which is useful in order to follow the process of pulping, lacks adequate precision for the determination of trace quantities. The need for trace methods based on equipment of moderate cost to allow extensive analytical control of production and deposit in the environment led Brønstad and co-workers to the development of the differential-pulse-polarographic methods for the analysis of pulping products from the paper industry. A steam distillation/extraction procedure makes it possible to determine 9,10-anthraquinone at levels below 5 μg/ml in the black liquor matrix (although the recovery of the AQ in this extraction procedure is rather low ∿ 60 %). Experiments to improve the present method further, especially for applications to paper, pulp and pulping materials and industrial sewage samples, are in progress according to these authors[47].

We used differential-pulse-polarography for the determination of AQ and non-quinoid additives in the black liquors of our in situ voltammetric measurements (see section III.2.3).

(II). POTENTIOMETRIC DETERMINATION OF REDOX POTENTIALS OF PULPING LIQUORS: GLUCOSE CARBOHYDRATE MODEL COMPOUNDS AND AQ-SYSTEMS

It is interesting to note that an electrochemical effect - the observation of a correlation between the delignification rates of amines[5] with the redox potential of the spent pulping liquor - provided the background for the proposed oxidation-reduction cycle mechanism of catalytic quantities of AQ for soda-AQ pulping[49]. There is now widespread agreement that AQ operates as a redox catalyst.

(II.1) Redox Potentials of Liquors

The reducing power of the liquor has always been of crucial importance in the eyes of Russian authors[50,51] (see also Galkin[54]). Measurements of the redox potentials of pulping liquors made at different stages of various hydrosulfite and sulfite digestions using a Pt-electrode and a calomel reference electrode were first published by Enkvist et al[2] in 1957.

Fleming found the redox potential of kraft and soda liquors to be in the region of -0.56 V to -0.6 V (vs.SCE). These potentials were measured in the course of a study of reducing agents[52], of amine compounds[5], of nitrogenous redox catalysts[53] as additives for soda pulping and in the elucidation of the AQ soda pulping mechanism[49], and agreed with the value reported for kraft liquor by Enkvist. Most liquors are susceptible to air oxidation which explains - according to Fleming and Bolker[52] - the high potential of -0.4 V found by Enkvist[2] in soda black liquor samples. The reported redox potentials were determined using a dropping mercury electrode (DME)[5,52] (the DME cannot be used with kraft liquor because of the reaction of Hg with sulfide) or a smooth Pt-electrode[52] in a precooled (25 ± 0.5°C) liquor stream during all the cooks[52]. The change of the redox potential of soda liquor as a function of temperature and time, as it was measured in our laboratory using a pressure cell and a Pt-electrode, is shown in Figure 1.

The measuring of the redox potentials in situ under pulping conditions seems essential for various reasons.

Continuous measurements of the electrode potentials during the entire course of cooking show that the negative

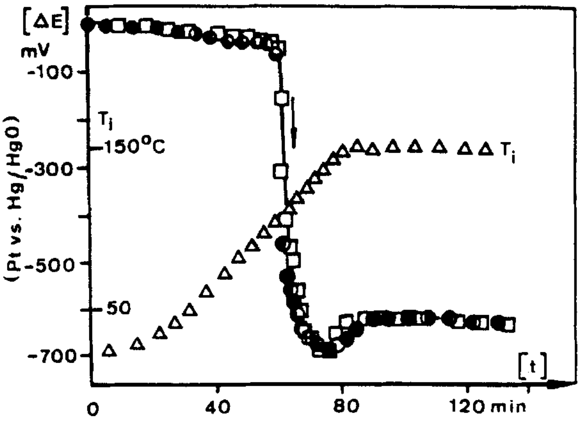


FIGURE 1: Change of the redox potential of soda liquor as a function of time (t) and applied temperature program (T_i Δ) measured in pressure cell (see Figure 7)

● soda cook of spruce wood

□ soda-AQ (+ 0.5 % on wood) cook of spruce wood

potentials cannot be associated with the lignin content as the negative potentials develop early in the temperature rise (see fig.1) before any lignin is dissolved. The negative redox potentials result from the presence in solution of reducing species, i.e. dissolved carbohydrates and their derivatives[5,49]. Blank cooks without wood chips showed a steady rise of the measured potential to + 0.5 V (vs.SCE) within 20 min[52] and remained constant thereafter.

It should be added here that Krunchak et al[56] have recommended the use of semiconductor glass electrodes for the determination of the oxidation potential of black kraft liquors as this type of electrode is not susceptible to poisoning by sulfides and dissolved oxygen.

(II.2) Redox Potentials of AQ - Sugar Systems

Spectrometric measurements in 0.1N sodium hydroxide solutions made in presence of anthraquinone-monosulphonate

(AMS), hemicellulose and beech Bjorkman lignin (MWL) by Iiyama et al[57] show that AMS is mainly reduced by carbohydrates to reduced AMS (AH_2MS), but not by lignin; the reoxidation of AH_2MS is mainly caused by lignin.

Anisimova et al[58,59] observed a rapid fall of the potential similar to that discussed above within the first minutes (the temperature used were: 30, 40, 50, 60 and 80°C) when adding glucose to 1N sodium hydroxide. Equations for the oscillations of the redox potential appearing during the heating of glucose in alkali were derived and discussed. The amplitude depends on the applied temperature. Fleming[37] has also observed an oscillation of the potential while measuring black soda liquor samples. Chupka et al[60] also noticed an oscillation of the redox potential while heating lignin model compounds in alkaline media.

The potentials for galactose, fructose, glucose at pH 8.2 and 85°C[61] and also potentiometric titrations with $K_3Fe(CN)_6$ in 2.5 N NaOH at 80°C for xylose, arabinose, galactose and glucose[62] have been reported.

The changes of potential of glucose in 1N NaOH solutions at 30 to 80°C are very complex and proceed in several stages[59]. (The product of heating glucose in alkaline solutions contains $\sim$ 60 compounds formed by enolization, oxidation, dehydration, peroxy-radical formation and polymerization). The literature on the electrochemistry of glucose and other carbohydrates at higher temperature is limited. Bockris et al[64] reported briefly the anodic oxidation of glucose, cellobiose, cellulose, starch and sucrose in NaOH at 80 - 100°C.

The reduction of D-glucose and further carbohydrates in buffered solutions (pH 6.5 - 10) was studied polarographically by Cantor and Peniston[65]. The ability of various carbohydrates (glucose, cellobiose, cellulose) and lignin to reduce aqueous suspensions of AQ, or to oxidize the reduced forms in aqueous, oxygen-free 1N NaOH, using a smooth Pt-electrode was studied by Hocking et al[66]. Redox potential curves for glucose in 1N NaOH and KOH and also of cellobiose at 23°C vs. time were recorded. KOH produces slightly lower redox potentials. The asymptotic minimum potential for glucose in absence of AQ was -0.78 V (Pt, vs.SCE) (Alkaline glucose solutions have less reducing power than dithionite solutions). Cellobiose was found to reduce AQ slowly (-0.75 V, Pt, vs. SCE) at room temperature, but rapidly at 50°C. The redox potential of AQ-hydrocellulose in 1N NaOH was found to be -0.84 V (Hg vs.SCE), the full reduction occurring at 100°C.

The actual potentials under true alkaline pulping conditions are not yet known and, therefore, experimental methods which could help in this case would be "very valuable from the practical and theoretical point of view"[67].

(II.3) Influence of Additives on the Redox Potential of Liquors

Fleming et al[49] found that the redox potential of liquor fell immediately below that of the control by about 60 mV on addition of AQ. Fleming et al[49] observed that for discrete samples of liquors momentarily exposed to air during sampling, the potential of the soda liquor rose rapidly to about -0.6 V (Pt, vs.SCE), whereas the AQ liquor remained stable at -0.74 V. We could not duplicate this effect with our electrode system (see fig.1). These authors also observed that certain organic amines, which are not themselves reducing agents, altered the redox potential of soda liquor during the cooking. The end-groups of dissolved carbohydrates are a likely source of reduction power in soda liquor. In the case of amine compounds the reducing agents may be the product of some interaction between amines and the wood components that dissolve early in the cook. A correlation coefficient of 0.8 for the redox potential versus the residual lignin concentration (%) on o.d. wood after 2 hr cooking time at 166°C leads to the reasonable conclusion that the pulping rates of alkaline liquors examined may be related to their reducing potentials at the end of the cook[5].

(III). POLAROGRAPHIC AND VOLTAMMETRIC STUDY OF QUINOID AND NON-QUINOID PULPING ADDITIVES AT AMBIENT AND MID-RANGE TEMPERATURES (90 ± 10°), AND UNDER PULPING CONDITIONS AT 150°C IN SITU

The high rate of AQ delignification is associated with the high reduction potential of the blow liquor. The common property of quinones and related cyclic keto compounds[68,69] or phenazines[53,70], discovered so far as catalysts for alkaline pulping, is the ability to cycle through reduction - oxidation reactions.

Fleming has divided catalysts into 2 categories: (i) those which are known to (or could conceivably) be converted into AQ in the strong alkaline, oxidizing-reducing pulping liquor (examples are: anthrahydroquinone; oxanthrones; di-, tetra-, hexa-, octahydro-AQ and anthrone) and (ii) those which, while unrelated to AQ, are alkali-stable and undergo reversible redox reactions[37].

Besides the alkaline stability, what are the attributes which distinguish a good catalyst such as AQ from a mediocre one (such as phenazine e.g.)? These attributes include, according to Fleming et al[55]: stability in hot pulping liquor; electrochemical reversibility; the normal potential; steric hindrance, and also, as was shown recently dianion formation[78], solubility of the oxidized form[71] and xylophilicity[72].

Of the 7 factors mentioned, 2 are of electrochemical nature, namely the electrochemical reversibility and the normal potential. As will be shown in this chapter, the solubility and the stability of additives can also be studied in situ by adequate electrochemical (voltammetric) methods.

Electrochemical reversibility is an important requirement for a catalyst which must cycle between oxidation states. The rapidity of the cyclic reaction of AQ accounts for the increased pulping rate.

The general scheme of the redox cycle is well established, but the details of the electron transfer and, therefore, also of the reversibility of the reaction under pulping conditions are still under investigation.

(III.1) Potentiometric Measurements

On the basis of the cyclic redox mechanism it seems only natural to correlate the normal potential (E^o) of an additive with its pulping efficacy. In fact, plots of some pulping data for various quinoid additives (also published by Holton[68]) versus their normal potential taken from the literature do show some kind of correlation (Figure 2).

Lindenfors[67] found a linear correlation between a log plot of kappa permanganate-values and E^o for linear quinones. E^o is by definition the potential at pH 0 and 50 % oxidation (measured versus the normal hydrogen electrode), conditions which are quite different from those during a soda cook. As shown by Conant et al[74], there is no linear dependence of the potential over the entire pH range.

(III.2) Polarographic and Voltammetric Determinations. Reduction-Oxidation Potentials of Additives and Mechanisms

In the past few years a great number of polarographic and voltammetric reduction-oxidation potentials

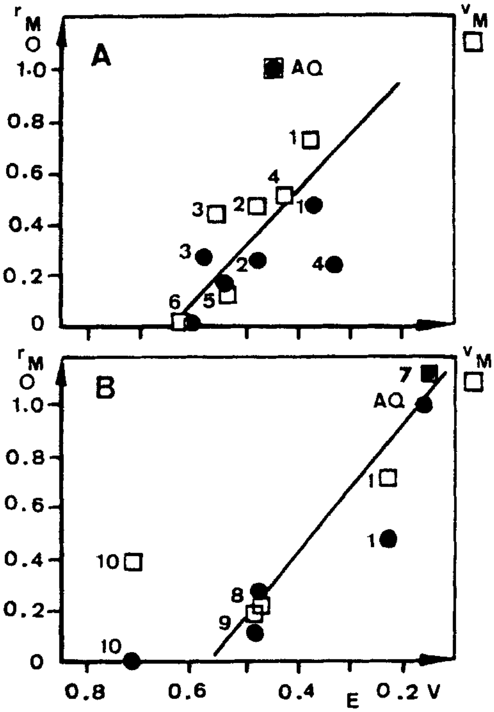


FIGURE 2: Normal potential values taken from literature versus delignification efficacy (r_M ●) and carbohydrate stabilization (v_M □)
A = values taken from Gill and Stonehill[73],
B = from Algar et al[43]
1 AMS; 2 1-OH-; 3 2-OH-; 4 1-Sulfo; 5 1,8-di-OH;
6 1,2-di-OH-anthraquinone; 7 2 - ethyl-anthraquinone;
8 9,10-phenanthrenequinone; 9 1,4-naphthoquinone;
10 1,4-benzoquinone

of potentially active quinoid and non-quinoid compounds have been published using dc-[38], ac-[38,53] or pulse-polarography[55,75] and cyclic voltammetry[76]. Landucci[77] proposed the use of cyclic voltammetry for the rapid screening of potential catalysts for oxidative delignification. Polarographic and structural comparisons of fluorenone - fluorenol with the anthraquinone-oxanthrone system and some similar, but inactive compounds led Eckert and Amos[78] to the conclusion that any diaryl carbinol could be considered as a potential catalytic system if criteria were met like: stability to pulping conditions; a reduction potential more positive than -1.2 V (vs.SCE) and the ability of the diaryl carbinol to form an anion at both oxygen and carbon under the conditions of alkaline pulping.

The experimental difficulties encountered in polarographic and voltammetric measurements in pulp chemistry are twofold:

First, the rather low solubilities at room temperature of most substances relevant to pulp problems in strongly alkaline solutions (1N NaOH). Therefore, soda pulping with anthrahydroquinone was proposed by Fullerton[79] to circumvent the solubility problem in commercial application. On the other hand, it has been shown that the optimum solubility for quinoid additives is about 0.40 ± 0.1 mg/l; higher solubilities may lead to lower xylophilicity[71].

Second, voltammetric measurements in 1N NaOH at temperatures above 140°C are quite difficult to perform due to corrosion and stability problems of the cell and electrodes used so that practically no work has been done in this field. (Rannev[80] in a recently published Russian monograph on "Chronopotentiographs" shows a sketch of a pressure cell with a rotating carbon working electrode, which apparently is in use in pulping work, but no details on the work performed in this cell are given).

(III.2.1) Measurements (Procedures) at Ambient Temperature

At room temperature the solubility problem of additives (quinoid and others) can be overcome principally either by chemical or technical means.

Chemical means usually used are the addition of organic solvents such as DMSO, DMF, dioxane, ethanol, etc. Thus Landucci[76] used DMSO in his cyclic voltammetric studies of quinoid additives, while Eckert and Amos used 50 % DMF for the study of fluorenone and various ketones[75,78]. But also the reduction of the sparingly soluble quinoid additive to its corresponding soluble hydroquinone has been employed. Commonly used reducing agents are $S_2O_4^{2-}$ (used by Fleming[38] and Hocking[66] in their ESR and electrometric measurements) or glucose (Fleming[49]) and different sugars (Hocking[66]).

Two technical methods are employed (i) Thin-layer voltammetry: Ksenzhek et al[81] employed for their investigations of the redox properties of quinoid compounds (benzoquinones and anthraquinones) over a pH range from 0 to 14 thin-layer voltammetry on pyrographite electrodes (see Figure 3).
Ksenzhek has shown that AQ can exist in four different forms, one oxidant (AQ), one intermediate ($AQ^{\cdot -}$, ion radical or semiquinone) and two reductants (AQH_2 and AQH^-). The fully reduced form can dissociate to AQ^{2-} at very high pH, but this ion was not mentioned. This may be due to the high ionic strength used in the experiments. In a soda cook, however, one has to expect such high ionic strength[67]. The dark red solution of AQ at 100°C formed in the early stage of pulping is due to the formation of the dianion[66,82,83,84,85], while the radical anion is said to be colorless or, at most, pale yellow[66].

We have used a modified thin-layer cell (developed by Schmidt[86]) for the determination of the reduction/ oxidation potentials of soluble and sparingly soluble quinoid compounds in 1N NaOH at ambient temperature[87]. While Ksenzhek[81] forms a film of the substance under study by applying the compound dissolved in an organic

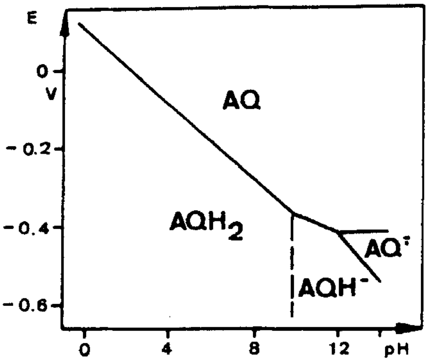


FIGURE 3: Relation between potential (E) and pH for different forms of anthraquinone[81].

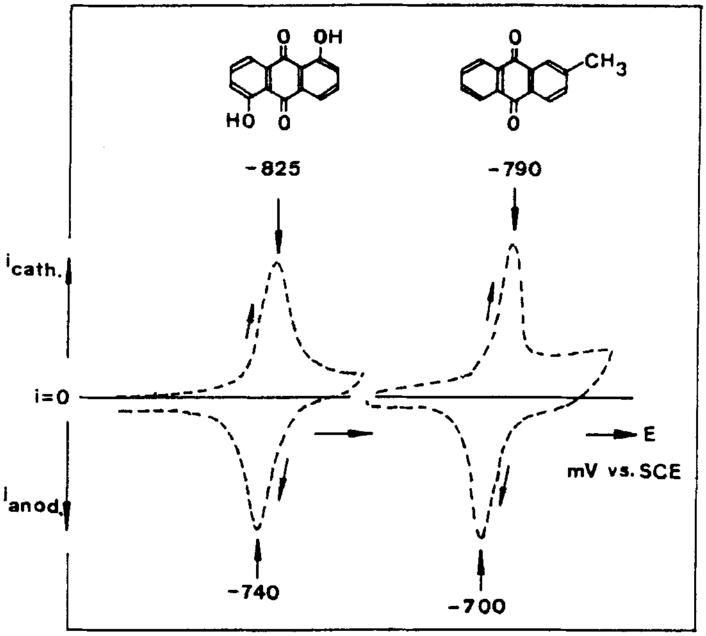


FIGURE 4: Thin-layer voltammograms of the soluble 1,5-di-OH-anthraquinone and the sparingly solved 2-methyl-anthraquinone measured in 1N NaOH, 23°C (layer = 35 μm)

solvent on the pyrographite electrode and evaporating the solvent subsequently, we measured the dissolved or finely suspended products in a 35 µm layer of 1N NaOH.

Figure 4 shows the well formed reduction and oxidation peaks of the sparingly soluble 2-methyl-AQ and the soluble 1,5-dihydroxy-AQ.

The limitations due to the poor solubility of the anthraquinone compounds in aqueous solutions (but whose reduction products are soluble) can be circumvented by dissolving these organics in the matrix of a carbon paste electrode itself as was first reported for AQ in 0.1 M Na_2CO_3 by Kuwana and French[88]. We have determined - using carbon paste electrodes - the reduction potential of a great number of candidate pulping catalysts some with very low solubilities in 1N NaOH such as di-chloro-, di-methoxy- or di-amino-AQ. Examples are given in Figure 5.

(III.2.2) Polarographic and Voltammetric Measurements at 90 ± 10°C of Additives in Presence of Wood

Another way to overcome the solubility problem is to use spruce wood as reducing agent instead of $S_2O_4^{2-}$ or any model substance as the reduced AQ form is usually soluble. This necessitates performing the polarographic or voltammetric measurements at higher temperatures as the reduction of the quinones to the soluble hydroquinone by the wood sets in only at higher temperatures. The reduction of AQ in situ is shown by polarographic and voltammetric measurements.

Figure 6 shows the appearance of the anodic current due to the oxidation of the reduced AQH_2-form for a temperature of 80°C.

Polarography or voltammetry in the alkaline aqueous media allows no distinction to be made between the semi-

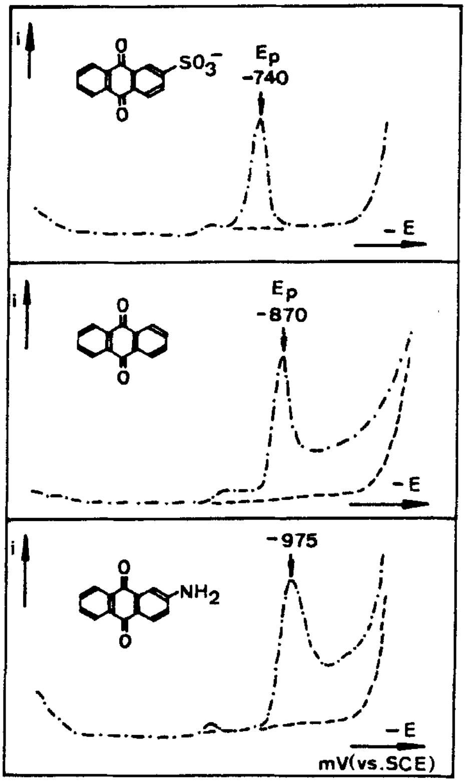


FIGURE 5: Voltammograms of different anthraquinones incorporated in a carbon-paste electrode measured in 1.25N NaOH, 23°C.

quinone from AQ and the anion or dianion (Fig.6) and, therefore, we refer to them collectively as "reduced AQ" or AQH_2 as was proposed by Fleming[38].

According to Landucci[76] the cyclic voltammetric examination of anthraquinone redox systems indicates that the corresponding semiquinone has at best only transient existence. The concentration of the radical in the pulp medium measured at 25°C was too low to be observed by ac-polarography, but it was readily detected by ESR

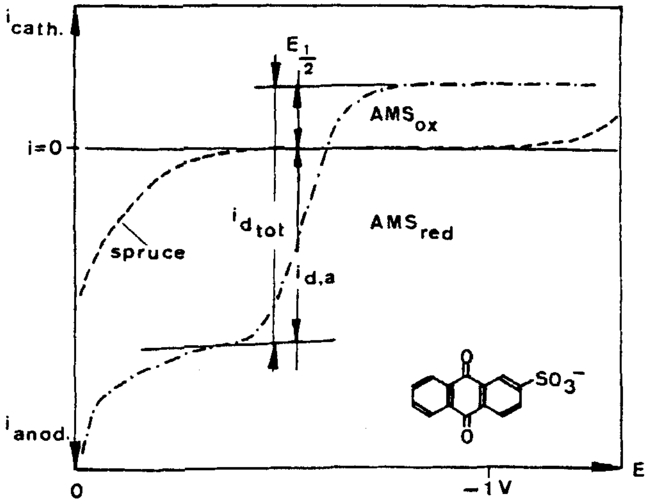


FIGURE 6: Dc-voltammogram of AMS measured at a hanging Hg-drop electrode in 1N NaOH / spruce at 80°C; $i_{d,a}$ = anodic current.

under pulping condition (kraft-AQ and soda-AQ) up to 150°C[3]. Fleming[38] gives a region of 97 - 120°C for the reduction of the AQ during the rise of the temperature of a digester (not isothermal). Our measurements show (see also measurements in the pressure cell (III.2.3)) that for AQ noticeable dissolution starts at about 75°C while the reduction of the AQ by the carbohydrate materials dissolved out of the wood sets in at about 80°C (isothermal). This temperature might depend on the wood species used. We have measured over 40 compounds at 90 ± 10°C using a hanging stationary mercury drop electrode and a modified rotating glassy carbon electrode in 1N NaOH in presence of spruce chips using dc- and ac-voltammetry. Such voltammetric measurements provide interesting information on reduction-oxidation potentials (see Figure 10a), on the temperature at which dissolution of the oxidized form and reduction start, on the amount of the reduced and oxidized form present at temperatures of 90 ± 10°C, on the stability of both forms etc., but no information on the delignification step is to be obtained from these mid-range temperature measurements in situ. This observation is in agreement with ac-polarographic results published by Fleming[38] and our subsequent measurements in situ at temperatures up to 150°C (vide infra (III.2.3)). Fleming incorporated a polarographic cell into the recirculation line of a 20-liter digester to monitor AQ reactions during soda-AQ pulping. However, for experimental reasons he had to cool down the black liquor before performing polarographic measurements. The question is whether this change in temperature would alter the experimental response or not. According to our experiments at 90°C in situ, it was quite obvious that only measurements at higher temperatures, if possible at or close to the pulping temperature, could give any conclusive information on reduction-oxidation potentials of the different additives and also on the fate and mechanism of pulp additives in soda cooking.

(III.2.3) Voltammetric Measurements of Additives under Pulping Conditions in Situ at 150°C using a Pressure Cell

A special pressure cell was constructed, designed for pressures as high as 5000 kPa. For construction details, see Figure 7 and the experimental section (III.2.3.1).

The pulping temperature was limited to 150°C; above this temperature serious troubles occur due to corrosion and mechanical instability of the materials employed and due to decomposition of the reference electrode. Above this temperature an external reference electrode (see[89]) is necessary.

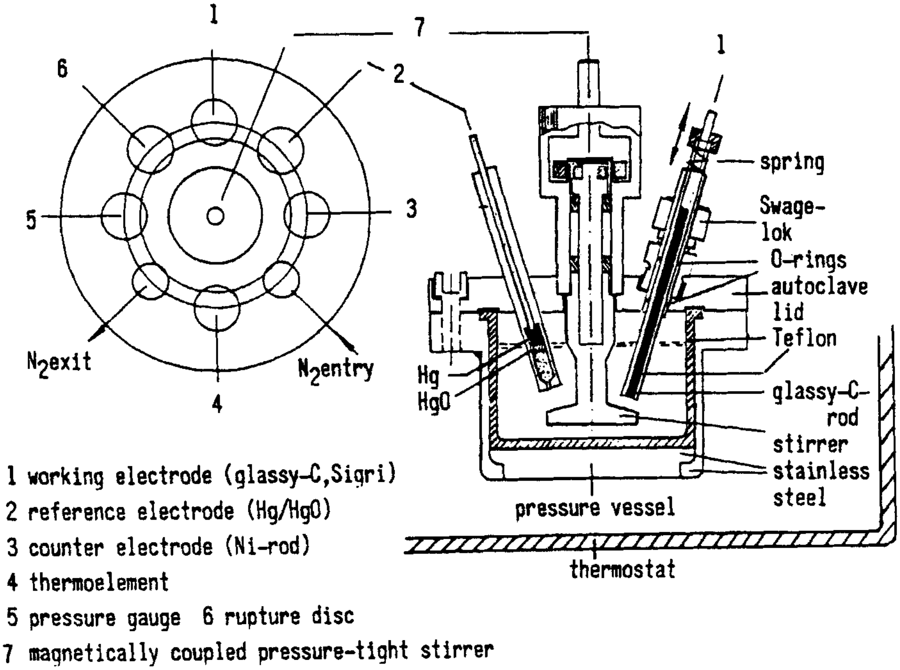


FIGURE 7: Pressure cell used for voltammetric measurements.

Dc-voltammograms recorded at different temperatures and different cooking times are shown in Figure 8. Only 7 out of 30 curves are depicted here.

The complete kinetic results of the soda pulping process with AQ monitored in situ by voltammetric measurements are plotted in Figure 9.

The picture (Figure 9) is in fair agreement with the concentration profiles and the current profiles of anthra-hydroquinone published by Fleming[38]. Also no increase of the anodic current occurred when pulping temperature was reached. Fleming pointed out that below 120°C nearly all AQ is reduced by the carbohydrates as is evidenced by the small gap between the

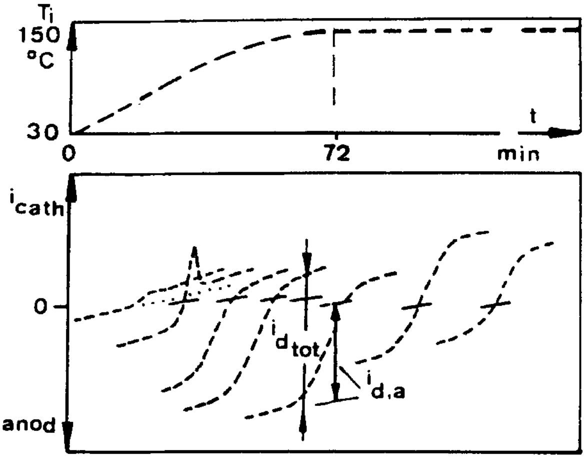


FIGURE 8: Voltammograms of anthraquinone measured at different temperatures and different cooking time in situ in 1N NaOH containing spruce chips.

total and the anodic current. Fleming found that at 120°C about 66 ± 12 % of the AQ charge was in the reduced form (AQH_2), the total amount in the liquor being 86 ± 15 %. Dissolution and reduction steeply increase up to about 135°C where a steep decrease of the anodic current ($i_{d,a}$) sets in. Above this temperature the difference between the total Faradaic and the anodic current increases indicating that the reduced anthraquinone is reoxidized by the delignification process. The maximum anodic current at about 125 ± 10°C corresponds to the glass transition temperature of the lignin and is thought to be the starting temperature for delignification.

Altogether over 20 additives have been looked at using the procedure described (III.2.3.1), including non-carbonyl catalysts such as phenazine, but also benzindazoldione, rosindone sulfonate, tetrabrominindigo and fluorenone.

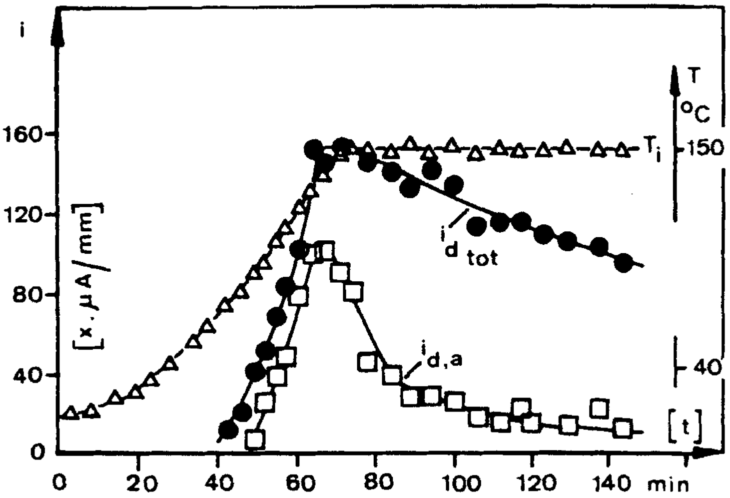
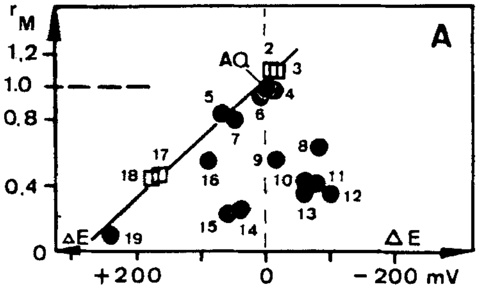


FIGURE 9: Current-time profiles of anthraquinone as a function of the applied temperature program ($T_i\Delta$) measured in 1N NaOH containing spruce chips. The circles stand for the total Faradaic current ($i_{d,tot}$), that is the sum of the reduction current of the dissolved oxidized form and the oxidation current ($i_{d,a}$) of the reduced AQ formed in the carbohydrate step.

All redox catalysts are assumed to function via a cyclic mechanism similar to that of AQ, although in most cases the active species have not yet been determined. The measurements in situ described here permit a better insight into this problem. Conclusions of mechanistic and theoretical interest in connection with the additive problems which are to be drawn from these measurements made in situ up to 150°C have been outlined earlier[6] and will be discussed in detail in further papers.

Concerning the polarographic and voltammetric half wave ($E_{1/2}$) and peak-potentials (E_p) resp. no correlation between these values and alkaline pulping



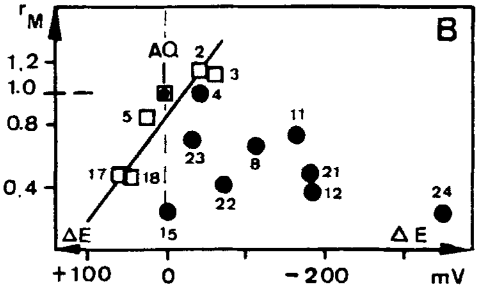


FIGURE 10a: A) Half-wave potentials vs. anthraquinone (ΔE) measured at 90°C in 1N NaOH/spruce versus delignification efficacy (r_M)

FIGURE 10b: B) Oxidation potentials of the reduced forms vs. anthraquinone (ΔE) measured at 150°C in situ in 1N NaOH/spruce versus delignification efficacy (r_M)

<u>2</u> 2-methyl; <u>3</u> 2-ethyl; <u>4</u> 2-NH_2-; <u>5</u> 2-CH_2OH; <u>6</u> 2-O-CH_3; <u>7</u> 2-CH_2OCH_3; <u>8</u> 1-NH_2; <u>9</u> 2,3-di-NH_2; <u>10</u> 1,2-di-NH_2; <u>11</u> 1,5-di-NH_2; <u>12</u> 2-OH; <u>13</u> 1-$NHCH_3$; <u>14</u> 1,8-di-NH_2; <u>15</u> 1-SO_3^-; <u>16</u> 1-$N(CH_3)_2$; <u>17</u> AMS; <u>18</u> 2-COOH; <u>19</u> 1,5-Diaza-9,10-AQ; <u>21</u> benzindazoldione; <u>22</u> phenazine; <u>23</u> rosindone-SO_3^-; <u>24</u> fluorenone.

activity is found. Figures 10a and 10b show the delignification efficacy (r_M) as defined earlier[91,63] versus measured potentials of different additives at 90°C and at 150°C. The squares in Figure 10a and Figure 10b indicate additives from Holton's original paper[68].

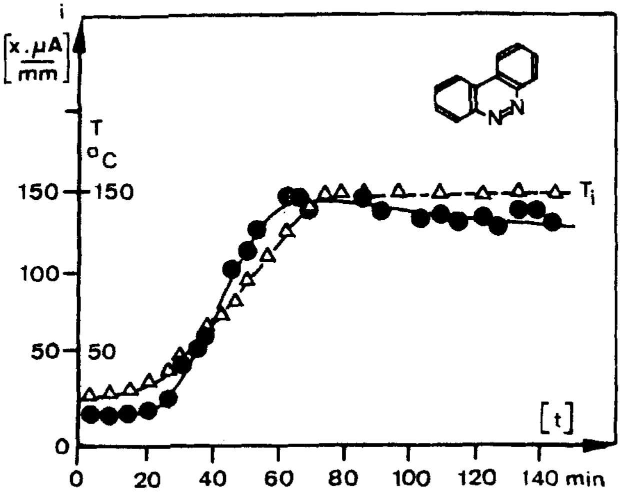


FIGURE 11: Current-time profile of benzocinnoline as a function of the applied temperature program ($T_i\Delta$) measured in 1N NaOH/spruce (see Figure 9)

It is evident that the correlation between the half-potential and the efficacy for these compounds is purely accidental. Eckert and Amos[75] found the same limitations in their polarographic work.

The fact that benzocinnoline - which shows a surprisingly negative reduction potential of - 1V (vs. SCE) at pH 14 - compared to -0.77 V (vs. SCE) works as a catalyst suggests, in the opinion of Fleming et al[55], that hot pulping liquors have lower potentials than those observed after cooling the liquor. No anodic current due to the oxidation of the reduced form could be determined under pulping conditions in the temperature profile (see Figure 11). The reason is probably due to the fact that the reduction power of the wood is in this case not sufficient to reduce detectable amounts. Benzocinnoline is about 1/40 as active as AQ on a weight basis[55]. One reason for inactivity of an additive is its failure to react with carbohydrates to establish one half of the catalytic cycle. We believe that an active additive needs a redox potential in the range of about -0.5 to -1.0 V (vs. SCE), which is the range between the oxidation of sugars from wood and the reduction of lignin active intermediates. According to Eckert[78], a potential catalytic system should have a reduction potential more positive than -1.2 V (vs.SCE) allowing the formation of the dianion.

Once this requirement is fulfilled, other factors like xylophilicity[72], solubility[71] and chemical stability are more important and will be discussed in subsequent papers.

Half-wave potentials do seem to be important as far as carbohydrate stabilization is concerned, high potential catalysts like AMS performing best[6].

(III.2.3.1) EXPERIMENTAL

Instrumentation: The working electrode 1 of the pressure cell (Fig.7) is a Sigri-Glassy-Carbon rod (3 mm diameter and 100 mm long, developed at Sigri-Research Lab., Meitingen, W.Germany) specially insulated and pressure mounted in fibre-reinforced (25 %) teflon. The surface of the working electrode is polished during the whole voltammetric experiment by periodically pressing the electrode on the rotating stirrer. This is essential as the glassy carbon electrode tends to be blocked at temperatures ∿ above 70°C. The severeness of the blocking varies with the additive under study, and we think that the blocking is most probably due to instability of the reduced additive form above 70°C.

As reference electrode 2, we use a modified mercury/mercury-oxide/NaOH electrode (see Figure 7) which is stable up to 150°C (see also[90]).

The counter electrode 3 is a highly polished Ni rod of 8 mm in diameter.

The direct-current dc-voltammograms were recorded with a Metrohm Polarecord E 506 and a Metrohm E 608 programmer. The voltammograms were run according to a preset program (scan time 210 sec) throughout the entire experiment (heating period: 20 to 150°C in 72 min, then 78 min at 150 ± 2°C (see Figure 9)) yielding about 30 curves per experiment. The measurements were performed with stirring (1100 rev/min) of the deoxygenated liquor. The voltammetric parameters were: starting potential = 0 V; potential range = 1.5 V; scan = 10 mV/sec; dc-mode. During the experiment, the temperature of the liquor in the cell and the pressure were monitored. After each run the black liquor was polarographed (see chapter I.3) and the volume of the liquor measured.

Wood / liquor system:

The voltammetric solutions were prepared by adding equivalent amounts (8.10^{-4} mole/l) of the respective additive to 200 ml 1N NaOH. After dissolution or homogenization of the additive by sonication (3 min with Sonifier B 12, Branson Sonic Power Co, USA), 6 ± 0.05 g spruce chips were transferred to the voltammetric cell and treated for 2 further minutes by sonication. The liquor to wood ratio in the cell was 30:1. (All additives studied were the same as those in pulping cooks).

For the voltammetric and pulping experiments handmade, air-dried and carefully homogenized chips (thickness 1-3 mm) of Norway spruce wood (picea abies) were used.

DEFINITIONS AND SYMBOLS

(i) Electrochemical:*

Potentiometry E = f (c)

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* Classification and nomenclature of electroanalytical techniques, rules approved 1975, PAC 29 (Int. Union of Pure and Applied Chemistry); see also Bond[4]

E = potential; c = concentration; i = current;
(E) = applied potential; dc = direct current;
ac = alternating current

Polarography = study of relationships between electric current and applied electromotive force or electrode potential with a liquid electrode whose surface is periodically or continuously renewed. The most common polarographic indicator electrode is the classical dropping mercury electrode (DME), but this definition comprises the use of dropping electrodes of other metals or liquid conductors.

Voltammetry = study of relationships between electric current (i) and applied electromotive force or potential with stationary such as hanging drops and pools and solid electrodes regardless of the material from which these are made.

Electrometric Techniques employed in Pulp Chemistry:

dc-polarography = direct current polarography

ac-polarography = alternating current polarography

SQW-polarography = Square-Wave-Polarography

Cyclic-voltammetry = triangular-wave-voltammetry

DPP = Differential-Pulse-Polarography

DPV = Differential-Pulse-Voltammetry

Symbols:

E^o normal potential

$E_{1/2}$ half-wave potential (dc-pol. and dc-voltammetry)

E_p peak potential: cyclic voltammetry; ac, SQW, DPP; DPV

For reversible systems:

$E^r_{1/2} = E^o + RT/nF.\ln Ox/Red$

organic polarography:

$$E^{r}_{1/2} = E_{1/2} \pm \frac{RT}{nF} \cdot \ln K_a \pm \frac{RT}{nF} \cdot pH$$

± takes into account whether a following or preceding chemical reaction occurs

$$E_{p,cycl.volt.} = E^{r}_{1/2} - 1.1 \frac{RT}{nF}$$

$$E_{p,ac} = E^{r}_{1/2}$$

$$E_{p,DPP} = E^{r}_{1/2} - 0.5 \, \Delta E_1$$

(ii) Pulping Parameters:

Delignification efficacy parameters:

r_o = relative efficacy vs. AQ at liquor-to-wood ratio $\lambda_w = 4$. Additive dose given in %wt./o.d.wood[91]

r_M = relative efficacy vs. AQ at liquor-to-wood ratio $\lambda_w = 4$. Additive dose given in moles/o.d.wood[91]

Carbohydrate stabilisation efficacy parameters:

v_o analogous to r_o

v_M analogous to r_M

Xylophilicity = affinity to wood[72]

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K_a = acidity constant; ΔE_1 = modulation amplitude

F = Faraday; n = number of electrons involved in the charge transfer step

and the technical aid of Mr.M.Schmid (Sigri), which made it possible to carry out these voltammetric measurements under severe conditions (150^{o}C, 1N NaOH), and also of Mr.H.G.Wenzel (CIBA-GEIGY) for technical assistance.

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